



Evaluation of Haloacetic Acid Concentrations in Treated Drinking Water

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Summary

i Reasons

The concentration of haloacetic acids (HAAs) in drinking water has been highlighted in a report to the European Commission as a possible future regulated parameter. However, knowledge of the levels of HAAs in the UK is limited and the available methodology is time-consuming and relatively expensive. Therefore, a study was commissioned to gather more robust data on the levels of HAAs in England and Wales as well as test and validate a new more rapid method recently developed in the USA.

ii Objectives

The general objectives of this project were as follows:

- The development and testing of the new rapid, robust method for the detection of nine haloacetic acids (HAAs) recently developed by the US EPA.
- Performance testing and validation of the developed method.
- Execution of seasonal surveys of HAAs in final drinking water at water treatment works in England and Wales.
- The collation of additional relevant data to aid the interpretation of the survey results.
- The preparation of a report including the method development and validation, the detailed results of the surveys and identification of possible implications for waters supplies in the event that a standard for HAAs is established.

iii Benefits

The purpose of this study was to gather more robust data on levels of HAAs in drinking water by conducting a representative survey of HAAs in drinking water in England and Wales. The results would help inform the UK negotiating position in the event of proposals for an EU standard or parameter. The development of a recently developed method for HAAs should also lead to a more rapid, robust and cheaper analysis should it become routine.

iv Conclusions

- The project represents the first use in the UK of the recently developed (IC)-MS/MS method for the detection of HAAs. This method proved rapid and stable.

- The results on 20 sites in England indicate that the 9 HAAs are detected at concentrations below those set as standard in the USA for 5 HAAs or below the concentrations suggested in the report of the review of the EU DWD for the 9 HAAs. The results obtained with the new method were similar to those seen in other recent surveys.

- In sites with higher levels of HAAs there is a tendency for seasonal variation with the lowest results being in the winter months with levels then increasing towards and peaking in summer.

- Higher levels were detected in samples from upland sites including those identified as having higher organic content.

v Recommendations

- For the complete validation of this method, it is recommended that multiple samples are collected from a few sites at regular intervals (e.g. monthly). This would enable the collation of statistically valid data for measuring the accuracy and precision of the new method.

- In parallel to this method development and its first use to detect HAAs at 20 sites, Cranfield University have been conducting a full seasonal survey of the same HAAs at the same sites. A full comparison of the concentrations detected by each method from samples taken at the same time is an important step and a unique opportunity in the potential use of the new method, and a chance to uncover any potential problem in its routine use.

1. Introduction

1.1 Objectives

The general objectives of this project were as follows:

- The development and testing of the new rapid, robust method for the detection of nine haloacetic acids (HAAs) recently developed by the United States Environmental Protection Agency.
- Performance testing and validation of the developed method.
- Execution of seasonal surveys of HAAs in final drinking water at water treatment works in England and Wales.
- The collation of additional relevant data to aid the interpretation of the survey results.
- The preparation of a report including the method development and validation, the detailed results of the surveys and identification of possible implications for water suppliers in the event that a standard for HAAs is established.

1.2 Background

The current EU Drinking Water Directive 98/83/EC (DWD) on the quality of water intended for human consumption came into force in 1998. Article 11 of the DWD makes provision for a review of the annexes, requiring a review of Annex 1 (the limit values) every five years and proposals for amendments, where necessary.

The first review in 2003 concluded it was premature to revise the Directive at that time, however the final report on the review of 2008 has now been published. Among the health related parameters to be identified through a drinking water safety plan (DWSP), or controlled by product specification were total haloacetic acids (HAAs) with a proposed parametric value of 80 µg/L. The European Commission has recently decided not to make revisions to the DWD at this point in time, preferring to concentrate on DWSPs and the monitoring of small supplies. However, the setting of a standard for HAAs is likely to be discussed further in the next few years.

Total haloacetic acids are calculated as the sum of the concentrations of nine HAAs (monochloro-, dichloro-, and trichloro-acetic acid, mono- and dibromo-acetic acid, bromochloroacetic acid, bromodichloroacetic acid, dibromochloroacetic acid and tribromoacetic acid). As the suggested value for total HAAs is likely to be discussed in the EU

it is important that the negotiating position of the UK be informed by data on the concentrations of these HAAs in drinking water.

There are data available from the USA where a standard for five HAAs has been in place but information for the UK is limited. A limited study in 2005 measuring slightly different HAAs than the US standard indicated the potential for high levels in UK drinking water with one region having a mean value above 80 µg/L (Malliarou *et al*., 2005). A further study by the same group indicated lower concentrations now being measured (Graham *et al*., 2009). Limited studies in Scotland and England measuring HAAs in drinking water have recently been completed (Parsons *et al*., 2009).

In 2009, Defra/DWI awarded contracts to both Cranfield University and WRc to undertake a survey of HAA concentrations in drinking water in England and Wales using both the current analytical methodology, and on the development, validation and use of a recent US EPA analytical method. As part of their contract, Cranfield University were charged with carrying out a literature review of the occurrence of HAAs in drinking water and to liaise with water companies to develop a seasonally-based survey of HAAs comprising four sampling sessions employing an established analytical method (GC/ECD).

WRc's involvement focused on the development and validation of an alternative rapid, robust analytical method for the determination of HAAs in drinking water based on the recent US EPA IC-MS/MS method. When the alternative method was available WRc collaborated with Cranfield University on some of the sampling occasions to provide survey samples which would be analysed using both methods.

Recent developments have been made in the USA (by US EPA in collaboration with Dionex) on the use of direct-injection Ion Chromatography (IC-MS/MS) for the detection of sub-µg/L levels of nine HAAs. In the UK, Severn Trent Laboratories (STL) had already carried out some preliminary development of this method. In addition, prior experience of the IC-MS/MS method by STL offered the possibility of reduced development costs. Because of this STL were sub-contracted by WRc to undertake the work on the development and validation of the alternative HAA analytical method.

2. Development of a Rapid, Robust Method for the Detection of Nine Haloacetic Acids

Current methods used in the UK water industry to determine haloacetic acids (US EPA methods 552, 552.1, 552.2 and 552.3 and ISO 23631 method) require solvent extraction, extract concentration and derivatisation (using hot methanol or diazomethane) followed by Gas Chromatography (GC)-µECD or GCMS detection. This is a rather long preparation involving extraction and derivatisation and subject to reliability problems.

Recent developments (by US EPA in collaboration with Dionex) have shown that a direct injection Ion Chromatography IC-MS/MS method can be used for the determination of the nine chloro- and bromo-haloacetic acids (US EPA Method 557, 2009). These methods allow separation and detection of sub-µg/L levels of nine haloacetic acids (HAAs) in high ionic strength matrices. Using this method, the analytes are separated from chloride, sulphate, nitrate, bromide and bicarbonate, and detected using a triple quadrupole mass spectrometer with an electrospray interface. Quantification is achieved using internal standards.

Ion Chromatography methods take advantage of the low pKa values of HAAs (~0.7–2.8) by using anion-exchange separation chromatography. Hydroxide based eluents are used in conjunction with chemical suppression, so the background signal entering the mass spectrometer is as low as that of water. Matrix ions are diverted to waste during the analytical run to avoid contamination of the detector.

IC-MS/MS methods are more efficient than traditional methods of analysis and can provide better quality data (precision and accuracy), due to fewer sample preparation steps. This type of methodology has the additional advantage of potentially being able to detect other DBPs such as iodinated substances, which are currently of interest due to the work of Plewa and Richardson (Plewa *et al*., 2004). It was recently used to develop a sensitive method for the measurement of perchlorate in drinking water and used in a monitoring survey for Defra (Blake *et al*., 2009).

There is current interest in Europe in this methodology and STL has been the first to investigate the use of this method.

The following section is the complete report written by McLaughlin, Kanda, Aslam and Oliver (Defra 8169) detailing the development and validation of the analytical methodology to determine haloacetic acids in potable waters using ion chromatography with electrospray tandem mass spectrometry. This work, based on the US EPA Method 557, has been developed and validated for the determination of nine HAAs in drinking water samples.

2.1 Introduction

Haloacetic acids (HAAs) are disinfection by-products produced in drinking water as a result of the reaction between free chlorine and bromide with natural organic matter, e.g. humic and fulvic acids. HAAs have been linked to possible human health effects and in the USA the Environmental Protection Agency (EPA) has established a Maximum Contaminant Level (MCL) of 60 µg/L for five HAAs (namely monochloroacetic acid (MCAA), monobromoacetic acid (MBAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA) and dibromoacetic acid (DBAA)) under the Stage I Disinfection Byproducts (DBP) Rule (US EPA, 1998). Stage II of the DBP Rule (US EPA, 2006) has maintained the MCL, but also requires a Minimum Reporting Limit (MRL) of 2 µg/L for MCAA and 1 µg/L for the other HAAs.

Other chlorinated or brominated HAAs that may be present in drinking water are as follows: chlorobromoacetic acid (CBAA); chlorodibromoacetic acid (CDBAA); dichlorobromoacetic acid (DCBAA); and tribromoacetic acid (TBAA).

In the USA, a method has been developed for the determination of all nine HAAs (Table 2.1) in water using IC-ESI-MS/MS. This is the basis of the method described below.

Table 2.1 Haloacetic Acids Determined by IC-MS/MS

Analyte	Chemical Abstracts Services (CAS) Registry Number
Monochloroacetic acid (MCAA)	79-11-8
Monobromoacetic acid (MBAA)	79-08-3
Dichloroacetic acid (DCAA)	79-43-6
Bromochloroacetic acid (BCAA)	5589-96-8
Dibromoacetic acid (DBAA)	631-64-1
Trichloroacetic acid (TCAA)	76-03-9
Bromodichloroacetic acid (BDCAA)	71133-14-7
Chlorodibromoacetic acid (CDBAA)	5278-95-5
Tribromoacetic acid (TBAA)	75-96-7

2.2 Analytical Methodology

2.2.1 Summary of the Method

Samples are preserved using ammonium chloride to prevent the formation of HAAs during storage. Prior to analysis, isotopically enriched internal standards (monochloroacetic acid-*2*-^{13}C, monobromoacetic acid-*1*-^{13}C, dichloroacetic acid-*2*-^{13}C, and trichloroacetic acid-*2*-^{13}C) are added to the samples. The sample is analysed by direct aqueous injection onto an ion

exchange column. Matrix components in the column eluate (e.g. chloride, sulphate and nitrate) are diverted to waste and the HAAs are directed into the ESI-MS/MS system. Acetonitrile is added post-column to enhance desolvation (in which the liquid sample is turned into an atomic gas) of the method analytes in the ESI interface. HAAs are detected using negative ion electrospray tandem mass spectrometry using multiple reaction monitoring. HAAs are quantified using internal standard calibration.

2.2.2 Reagents, Materials and Instrumentation

Standards and Reagents

HAA analytical grade standards (99% purity) were purchased from Sigma-Aldrich (Gillingham, Dorset, UK). Isotopically enriched internal standards (monochloroacetic acid-*2*-^{13}C, monobromoacetic acid-*1*-^{13}C, dichloroacetic acid-*2*-^{13}C, and trichloroacetic acid-*2*-^{13}C) were purchased from Dionex. Acetonitrile (HPLC grade) was purchased from Rathburn Chemicals (Walkerburn, Scotland, UK). Deionised water (18 megaohm-cm resistance or better) was prepared in the laboratory.

Equipment

- Dionex ICS2000 Ion Chromatograph with column heater and degasser
- Dionex AS50 Autosampler with 100 µL loop
- Dionex IonPac AG24 Guard Column, 50 x 2 mm id
- Dionex IonPac AS24 Analytical Column, 250 x 2 mm id
- Dionex Suppressor for anions, ASRS 300, 2 mm
- Agilent 1100 HPLC system with binary pump, degasser, column heater and valve
- Applied Biosystems API5000 MS/MS with electrospray interface

2.2.3 Preparation of Standards and Samples for Method Validation

Preparation of Standards

Stock solutions (1 mg/mL) of the nine HAAs (Table 2.1) and the four internal standards (MCAA[2-^{13}C], MBAA[1-^{13}C], DCAA[2-^{13}C] and TCAA[2-^{13}C]) were prepared by weighing 10 mg of the solid material into 10 ml vials and adding 10 ml of methyl tert-butyl ether (MtBE). (Stocks are made in MtBE because they are not stable in water and react with other solvents).

A mixture of nine HAAs at 0, 0.25, 1.0, 2.5, 5.0, 10.0 and 20.0 µg/L with four isotopically labelled internal standards at 4.0 µg/L were prepared in deionised water containing 100 mg/L of ammonium chloride. Ammonium chloride is added to all samples including distilled water standards (even though it is not required) and this is so that the residual chlorine present in drinking water samples is allowed to react with ammonium chloride to form chloramines, effectively preventing chlorine-mediated formation of method analytes during storage.

Preparation of Validation Samples

The method was validated by the analysis of duplicate samples of tap water containing 100 mg/L ammonium chloride. One set of duplicate samples was analysed at a low spiked concentration and another duplicate set was spiked at a high concentration. Duplicate blank samples (of deionised water and tap water) and a tap water sample spiked close to the expected limit of detection were also analysed.

- Low Spike (2 µg/L)
- High Spike (10 µg/L)
- Reagent Blank samples were unspiked
- Tap Water Blank samples were unspiked
- Tap Water Samples spiked close to the limit of detection (1 µg/L)

Preparation of Stability Samples

Samples to determine the stability of HAAs in tap water were prepared in 500 ml glass bottles which were filled with tap water containing 100 mg/L ammonium chloride and spiked with 20 µg/L of each HAA.

IC-MS/MS Analysis

Prior to analysis, each validation sample was spiked with the four isotopically- labelled internal standards at 4.0 µg/L.

A 2 ml aliquot of each analytical standard and validation sample was transferred to an autosampler vial for IC-MS/MS analysis.

The following IC-MS/MS conditions were used for analysis:

Table 2.2 IC-MS/MS Conditions for HAA Analysis - I

Parameter	Conditions
IC equipment:	**Dionex IC2000**
Column	Dionex IonPac® AS24 250 mm x 2 mm i.d.
Pre-column	Dionex IonPac(R) AG24 50 mm x 2 mm i.d.
Column compartment temperature	15°C
Column	Dionex IonPac® AS24 250 mm x 2 mm i.d.
Pre-column	Dionex IonPac(R) AG24 50 mm x 2 mm i.d.
Column compartment temperature	15°C
Hydroxide gradient	7 mM for -1 to16.8 minutes, then 18 mM for 16.8 to 34.2 minutes, then 60 mM for 34.4 to 51.2 minutes, then 7 mM for 51.4 to 56 minutes
Eluent flow rate	0.30 ml/minute
Suppressor	Dionex ASRS® 300 2 mm, external water mode
Matrix diversion divert windows	0 to 8 minutes, 16.5 to 21.2 minutes, and 33 to 39.2 minutes
Sample volume	100 µl loop
Run Time	59 minutes
Expected backpressure	1200 psi
Expected background conductance	<0.5 µS/cm
Matrix diversion time	0-5 minutes and 14 to 15 minutes
Mass Spectrometer	**API 5000**
Mode:	Electrospray ionisation (negative ion)
Curtain gas	20.00
CAD Gas	5.00
GS1	50
GS2	60

Table 2.3 IC-MS/MS Conditions for HAA Analysis - II

Analyte	Reactant Ion (m/z)	Product Ion (m/z)	Dwell time (mSec)	Periods	DP	EP	CE	CXP
MBAA	136.99	78.9	500	**MRM Period 1**	-55	-2	-42	-13
MCAA	92.9	35.1	500		-55	-2	-16	-15
MBAA-1-13C	138	78.9	500		-55	-2	-42	-13
MCAA-1-13C	93.9	35.1	500		-55	-2	-16	-15
DBAA	217.102	172.8	500	**MRM Period 2**	-55	-10	-12	-25
BCAA	171	78.8	500		-31	-5	-18	-11
DCAA	126.96	83	500		-45	-5	-12	-15
DCAA-2-13C	127.96	84	500		-45	-5	-12	-15
DBAA	214.7	170.7	500		-21	-4	-11	-5
TBAA	251.444	78.8	500		-30	-4	-34	-12
CDBA	206.8	81	500		-35	-4.5	-22	-13
TCAA	160.838	116.791	500	**MRM Period 3**	-15	-4.5	-22	-17
TCAA-2-13C	162	118	500		-15	-4.5	-22	-17
BDCAA	79	79	500		-35	-4.5	-22	-13
TCAA (2)	116.937	35	500		-55	-10	-18	-15
TCAA -2-13C 2	117.937	35	500		-55	-10	-18	-15
TBAA (2)	255	81	500		-55	-10	-18	-15
BDCAA (2)	163	81	500		-55	-10	-18	-15

2.3 Results

The mass chromatograms of a 20 µg/L analytical standard of the nine HAAs and the labelled internal standard are shown in Figures 2.1 to 2.9.

Calibration graphs of the nine HAAs are shown in Figures 2.10 to 2.18.

2.3.1 Method Performance

The method was validated by the analysis of duplicate samples of raw and final water at a low spiked concentration and another duplicate set was spiked at a high concentration. Samples were analysed using the methodology described above (Section 2.2) on six occasions. The performance data are provided in Tables 2.4 to 2.12.

2.3.2 Method Detection Limit

The limit of detection of each HAA was calculated using 3 x SD (the within batch standard deviation) of very low spiked tap water sample, which is in accordance with the requirements of the UK Water Supply (Water Quality) Regulations. Limits of detection of <1 µg/L were obtained for all 9 HAAs.

The calculated limit of detection is shown in Tables 2.4 to 2.12.

Figure 2.1 Mass Chromatogram of monochloroacetic acid (MCAA)

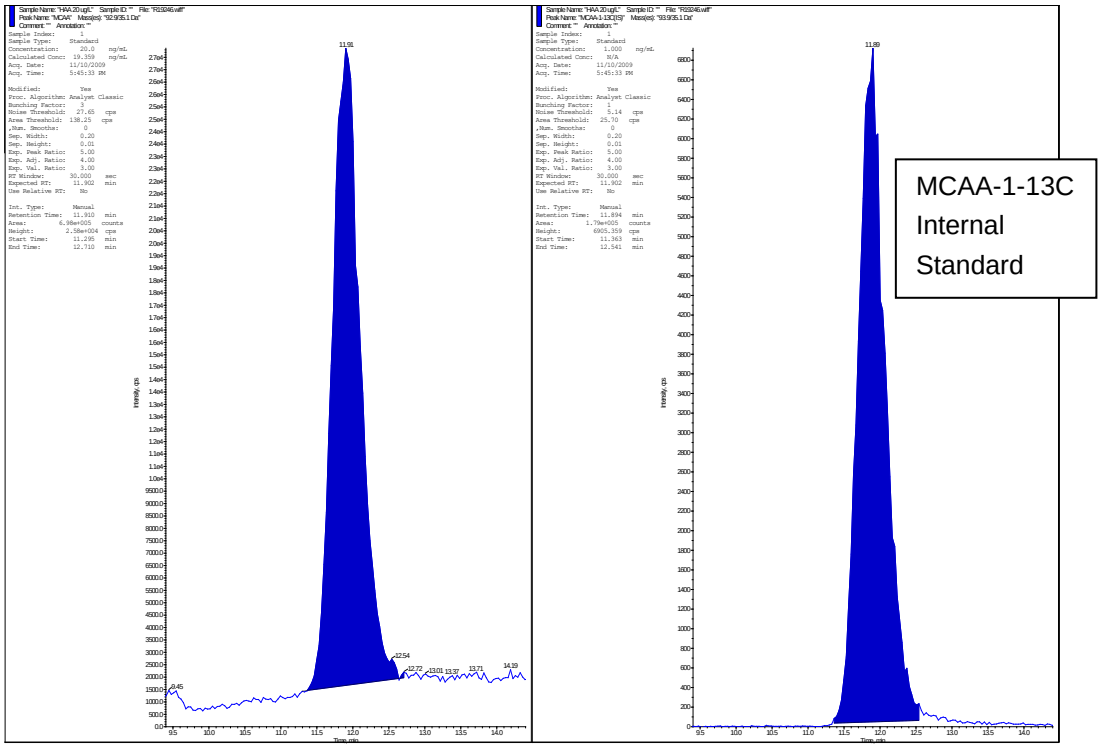


Figure 2.2 Mass Chromatogram of monobromoacetic acid (MBAA)

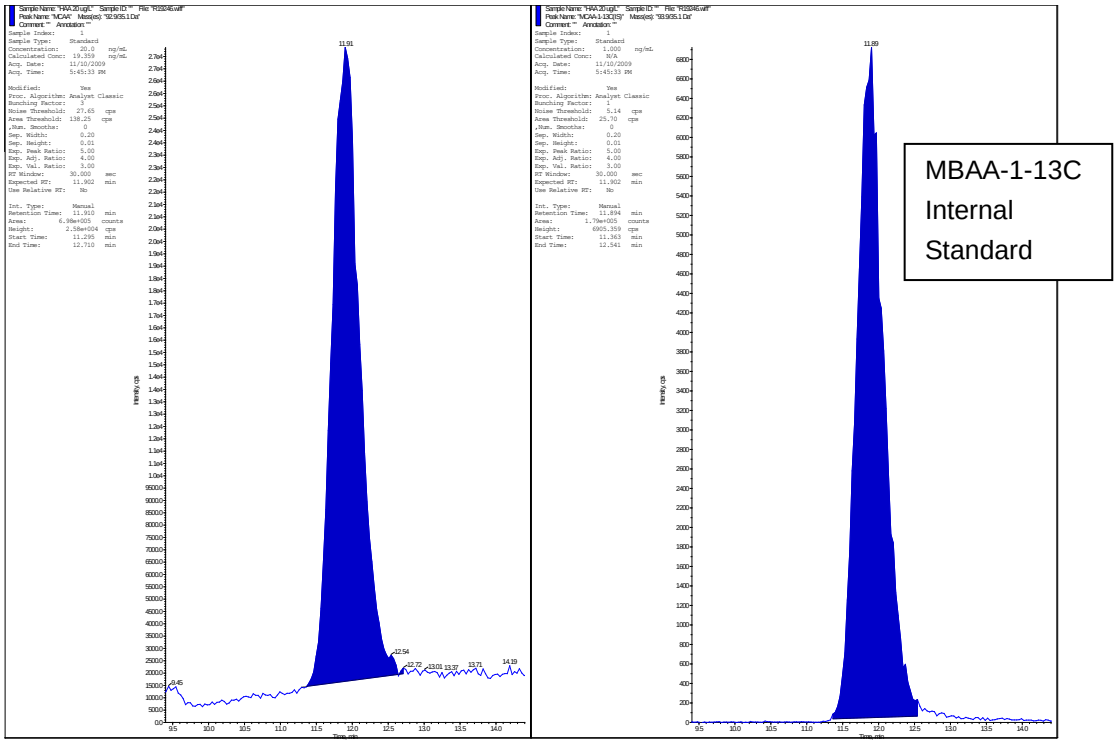


Figure 2.3 Mass Chromatogram of dichloroacetic acid (DCAA)

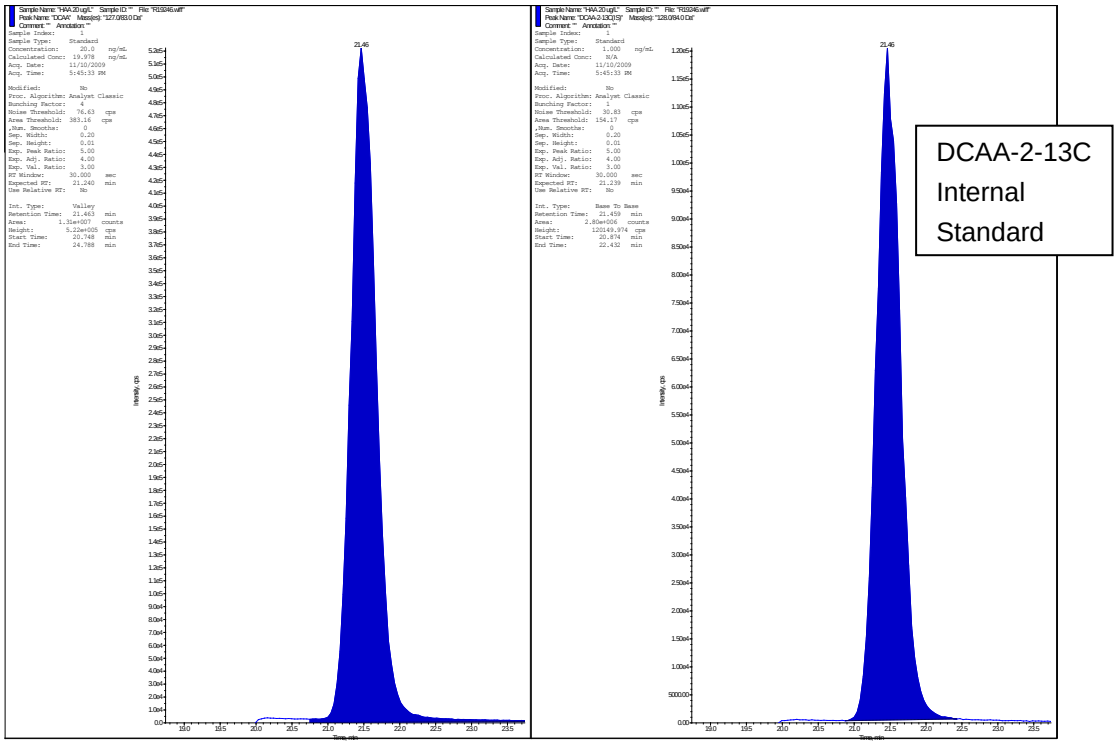


Figure 2.4 Mass Chromatogram of bromochloroacetic acid (BCAA)

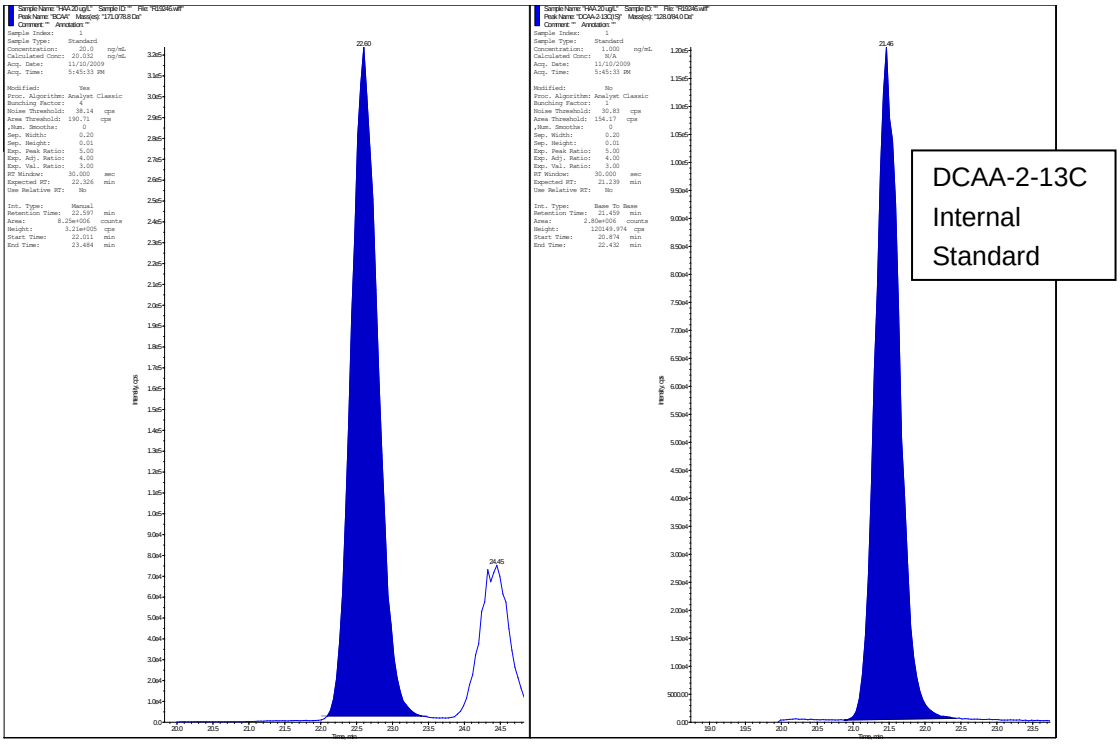


Figure 2.5 Mass Chromatogram of dibromoacetic acid (DBAA)

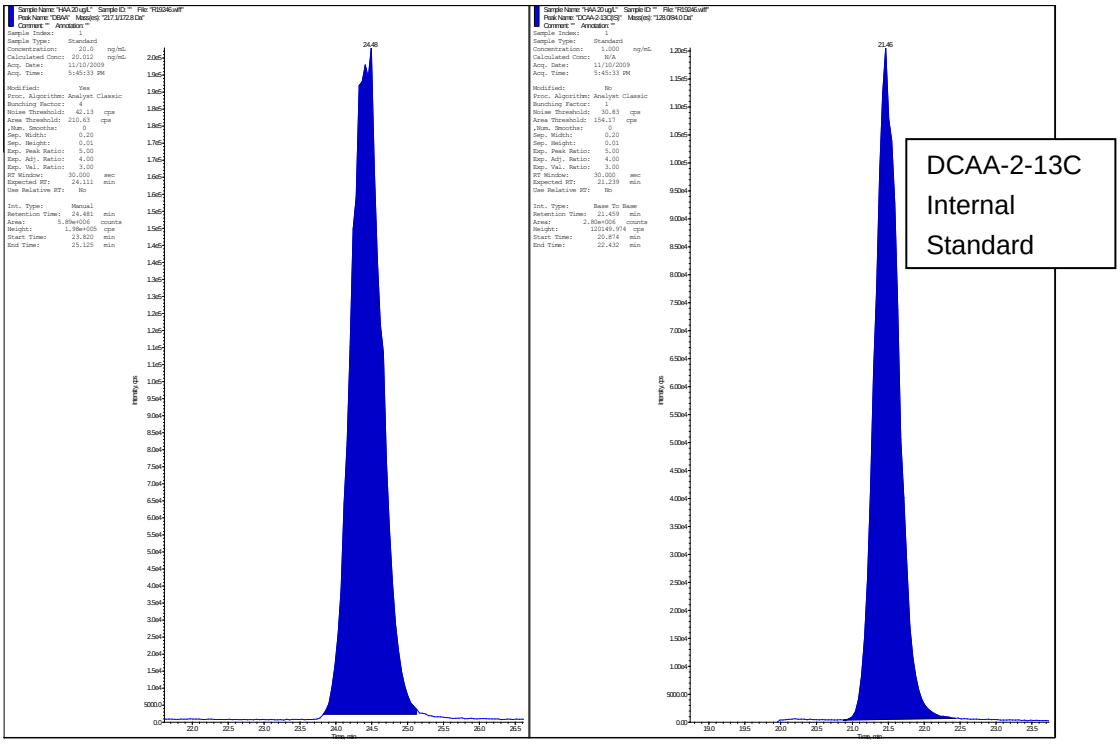


Figure 2.6 Mass Chromatogram of trichloroacetic acid (TCAA)

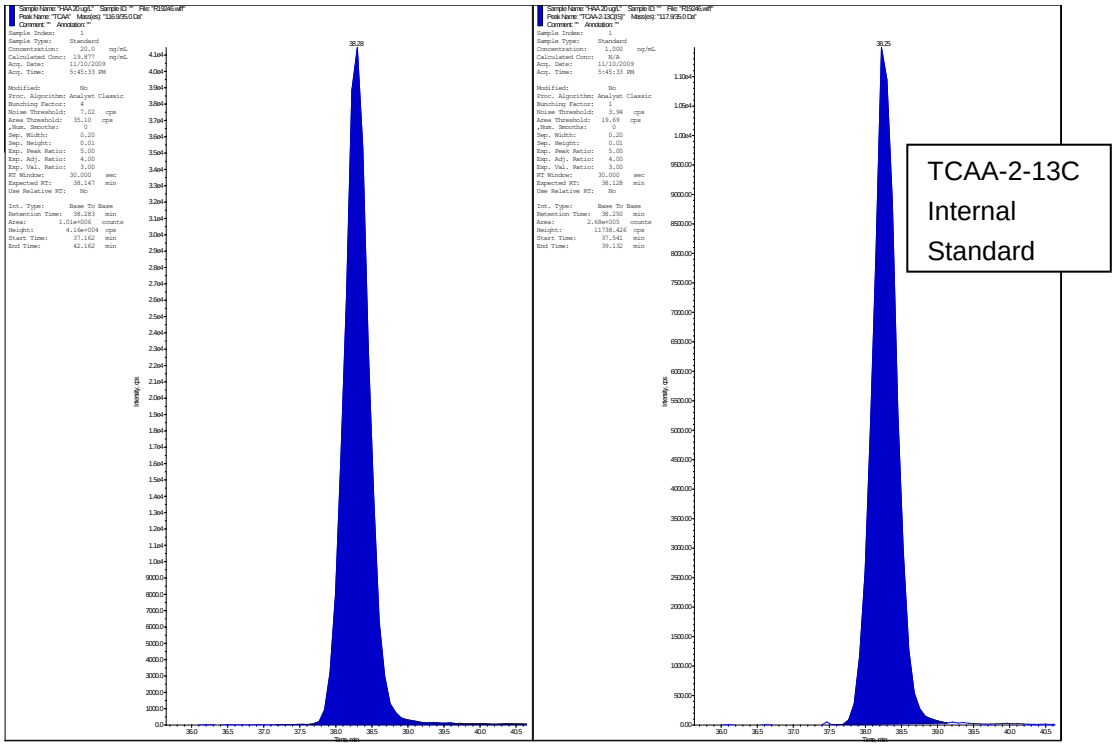


Figure 2.7 Mass Chromatogram of bromodichloroacetic acid (BDCAA)

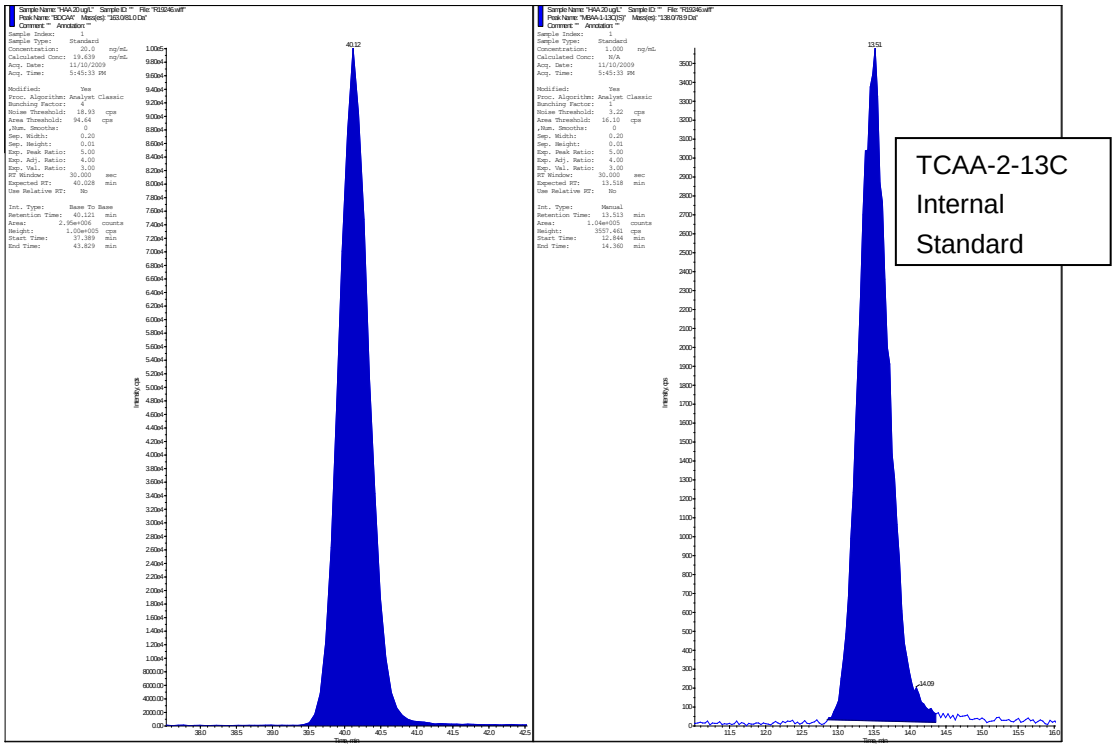


Figure 2.8 Mass Chromatogram of chlorodibromoacetic acid (CDBAA)

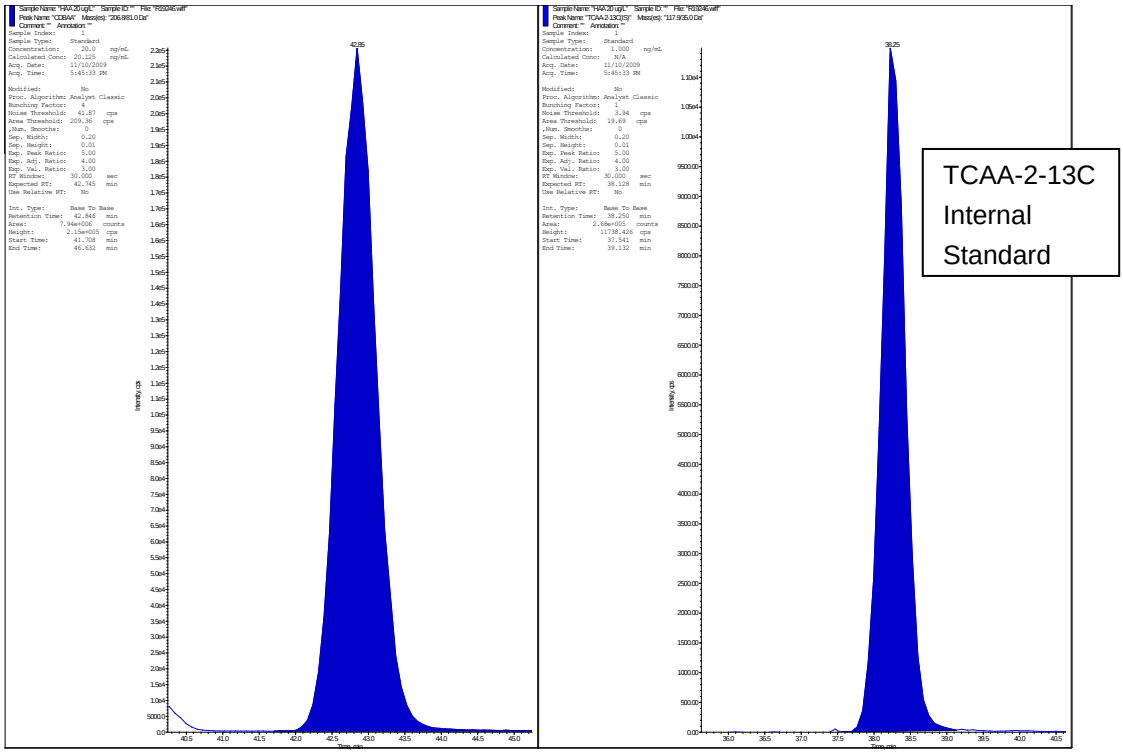


Figure 2.9 Mass Chromatogram of tribromoacetic acid (TBAA)

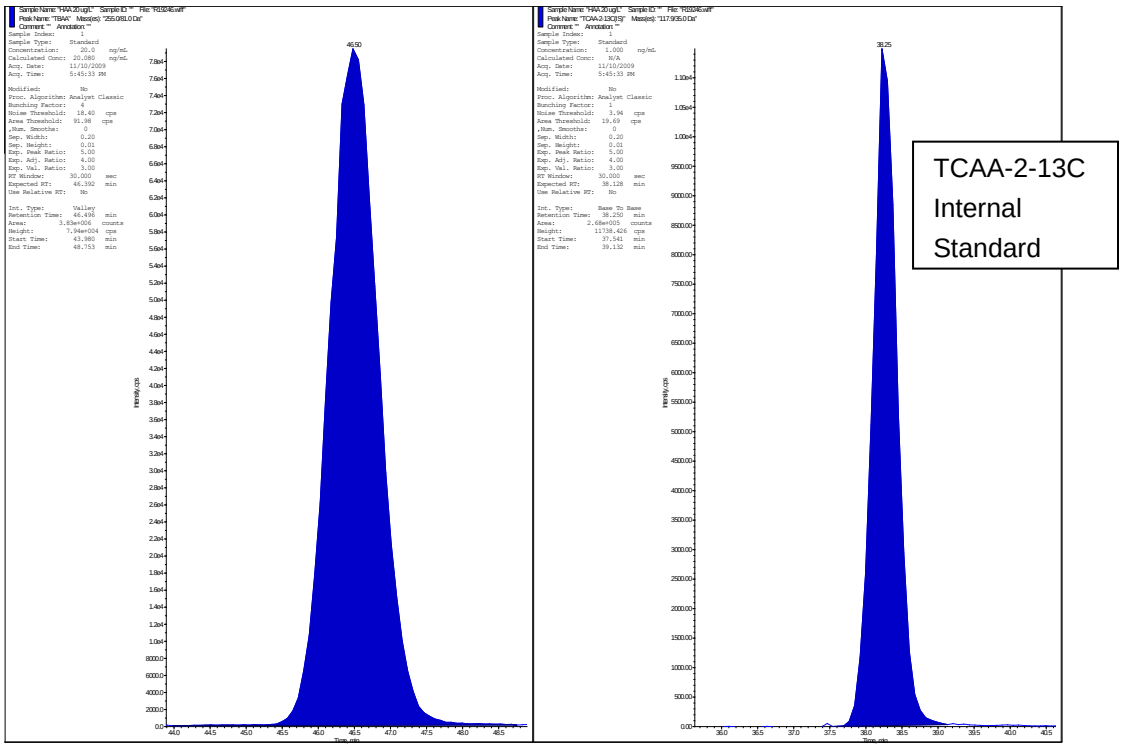


Figure 2.10 Calibration graph of monochloroacetic acid (MCAA)

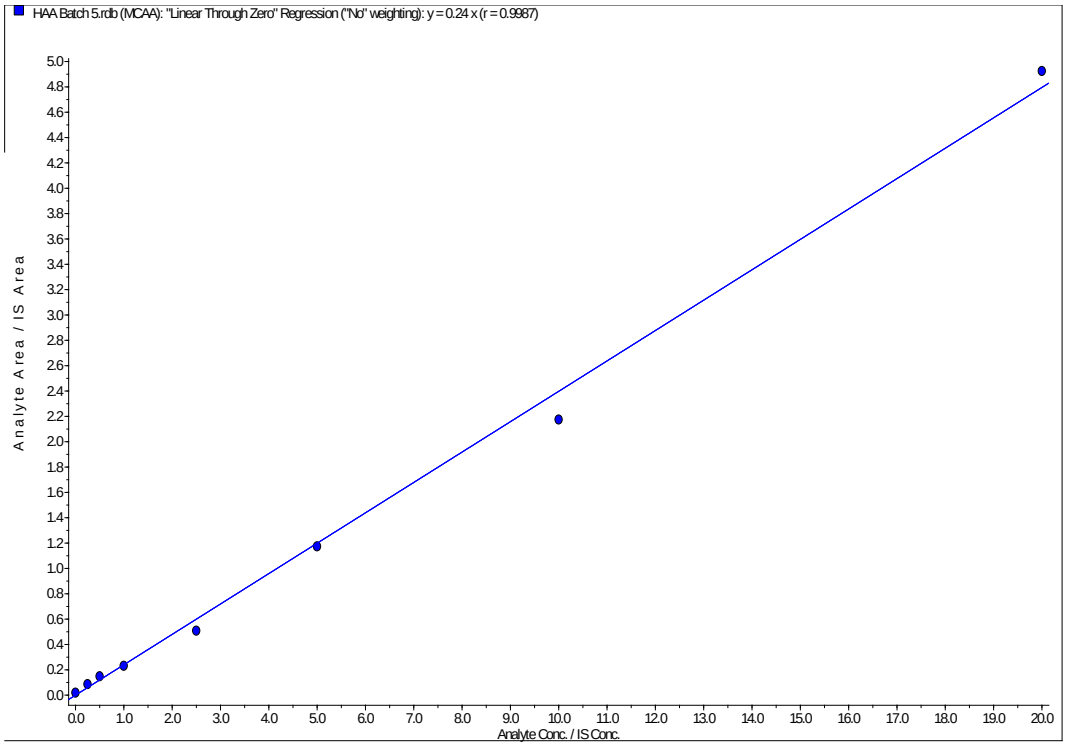


Figure 2.11 Calibration graph of monobromoacetic acid (MBAA)

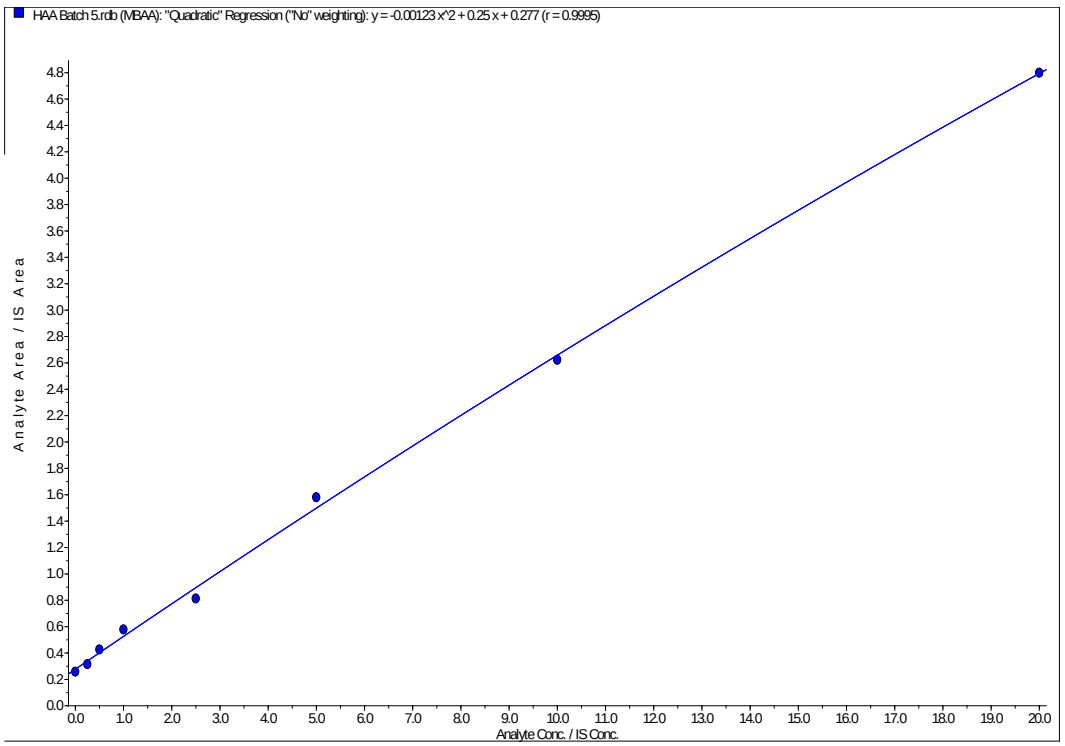


Figure 2.12 Calibration graph of dichloroacetic acid (DCAA)

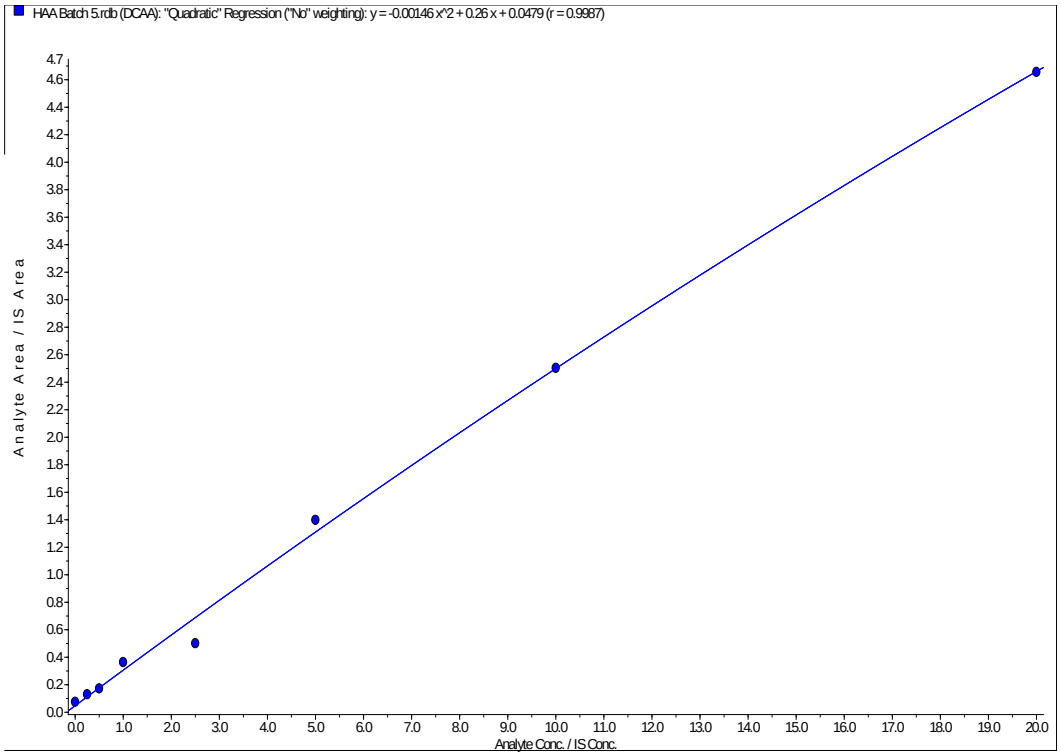


Figure 2.13 Calibration graph of bromochloroacetic acid (BCAA)

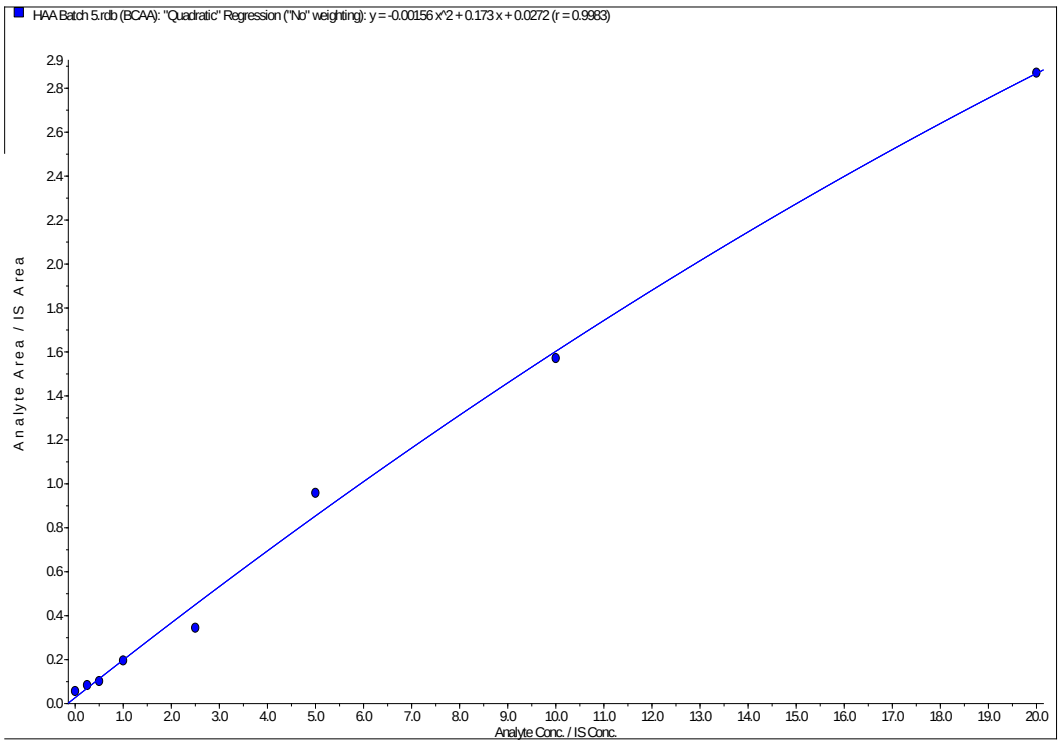


Figure 2.14 Calibration graph of dibromoacetic acid (DBAA)

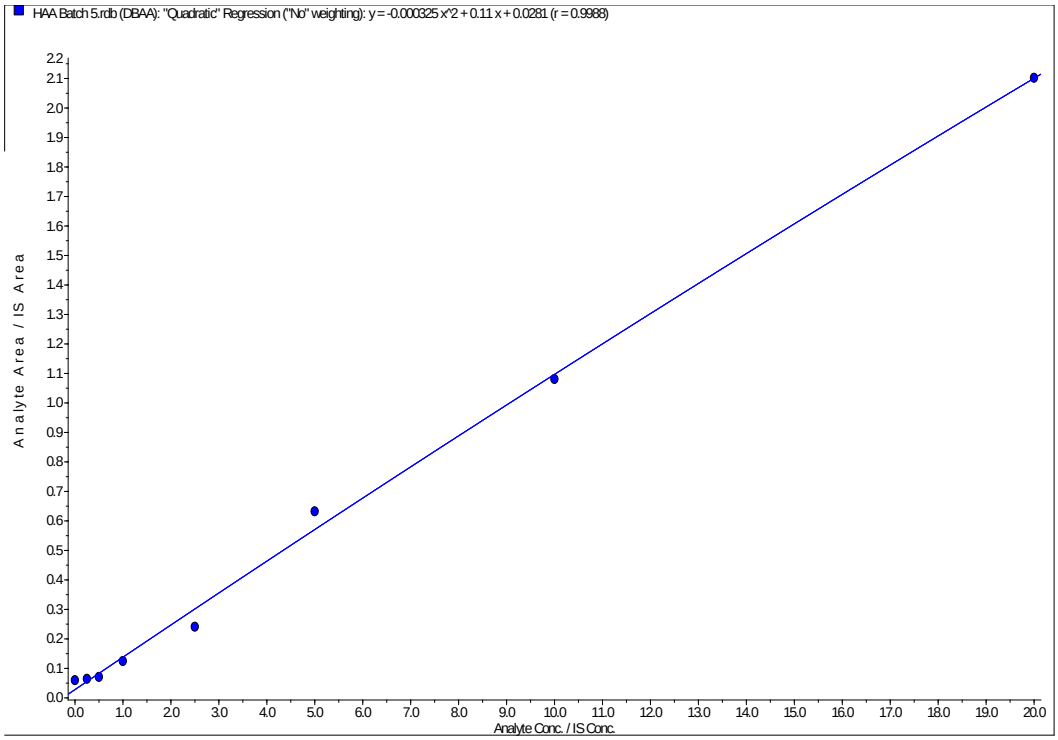


Figure 2.15 Calibration graph of trichloroacetic acid (TCAA)

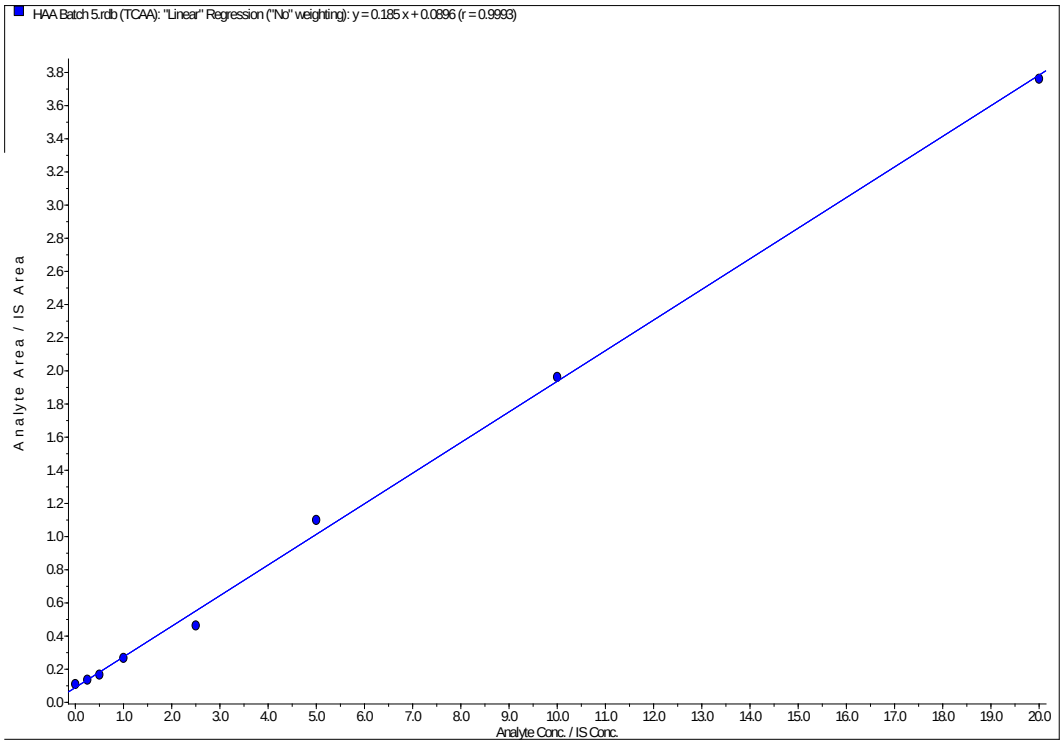


Figure 2.16 Calibration graph of bromodichloroacetic acid (BDCAA)

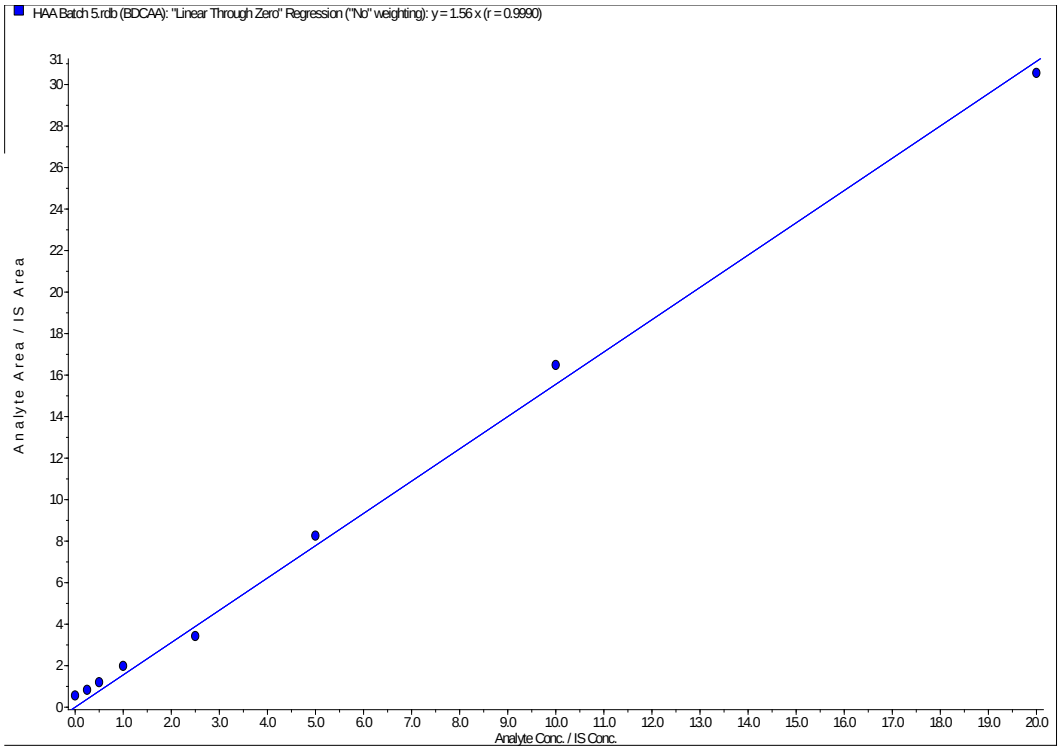


Figure 2.17 Calibration graph of chlorodibromoacetic acid (CDBAA)

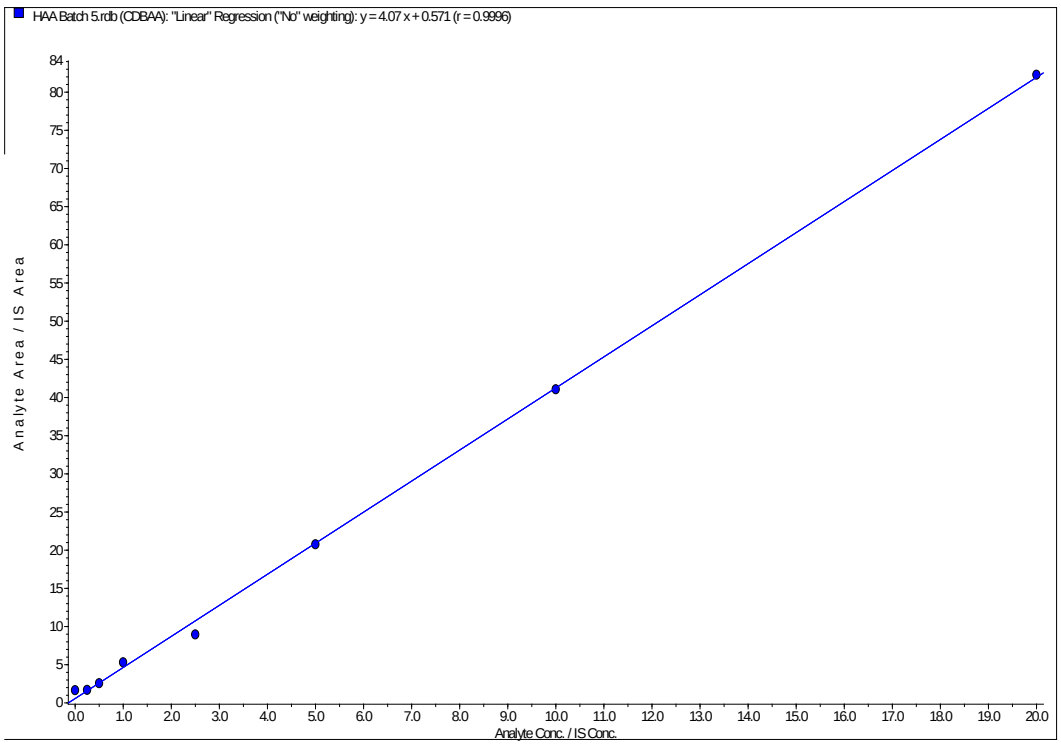


Figure 2.18 Calibration graph of tribromoacetic acid (TBAA)

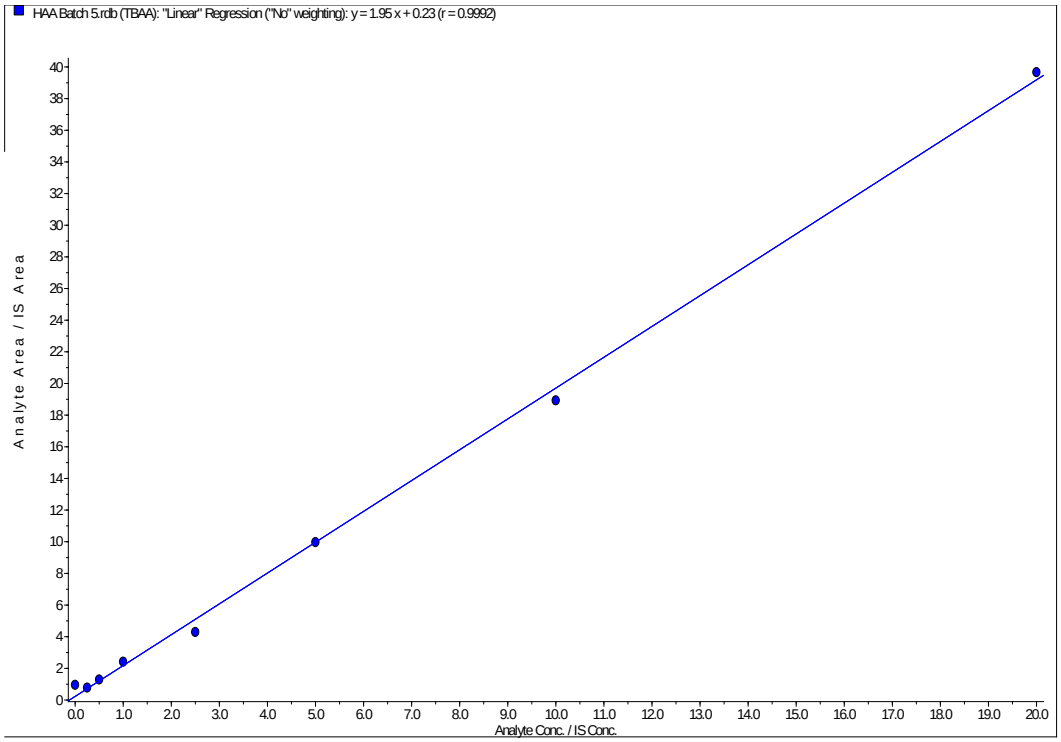


Table 2.4 Performance data of monochloroacetic acid (MCAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.0140	1.0630	0.0480	4.1590	14.4500
	2	0.0390	1.2080	0.0680	4.2120	15.2910
2	1	0.0090	0.8570	0.0500	3.6400	14.1910
	2	0.0100	0.9840	0.0470	3.8560	13.5410
3	1	0.0780	1.0380	0.2300	3.7510	13.6440
	2	0.0380	0.9930	0.0960	4.0110	14.0620
4	1	0.0100	0.4670	0.0100	3.2740	14.3410
	2	0.0100	0.4740	0.0100	3.7220	15.5980
5	1	0.0280	1.0510	0.1380	5.0250	16.7560
	2	0.0320	1.0780	0.0100	4.1390	17.1310
6	1	0.0440	1.0820	0.1190	3.7810	13.6340
	2	0.0640	1.2700	0.0380	3.6630	16.0030
Mean		0.0313	0.9638	0.0720	3.9361	14.8868
M1		0.0009	0.1330	0.0052	0.3022	2.5410
M0		0.0002	0.0063	0.0034	0.0931	0.7198
F value		3.964	21.198	1.501	3.248	3.530
Signif.		NS	***	NS	NS	NS
Sw		0.015	0.079	0.059	0.305	0.848
Sb		0.018	0.252	0.029	0.323	0.954
St		0.023	0.264	0.066	0.445	1.277
Rel SD (St)		74.61%	27.38%	91.13%	11.29%	8.58%
F 0.05		2.01	2.21	1.83	1.94	1.94
Calc. F		0.0000	0.0007	0.0000	0.0020	0.0163
Est Degs F		7	5	10	8	8
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.238**			
Bias						
Uncertainty					± 25.99%	± 24.56%
Recovery					**96.60%**	**92.59%**
SD of Mean Recovery			25.79%		9.55%	7.01%
Se of Mean Recovery			7.776%		2.878%	2.115%

MCAA Limit of Detection = 0.238 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square
M_0 = Within Batch Mean Squares
sw = Within batch standard deviation
sb = Between batch standard deviation
st= Total standard deviation

NS - Not Significant
* - Significant at the 0.05 level
** - Significant at the 0.01 level
*** - Significant at the 0.001 level
Pass St not significantly larger than target

Table 2.5 Performance data of monobromoacetic acid (MBAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.01	1.128	0.358	4.319	16.763
	2	0.01	1.095	0.376	5.054	17.45
2	1	0.01	1.44	0.11	5.15	17.152
	2	0.01	1.35	0.664	4.975	17.414
3	1	0.132	1.296	0.363	5.173	13.663
	2	0.368	1.294	0.823	4.736	14.152
4	1	0.01	1.433	0.085	4.64	17.398
	2	0.01	0.749	0.273	4.749	17.043
5	1	0.445	1.297	0.38	5.364	16.943
	2	0.084	1.307	0.579	5.107	17.259
6	1	0.01	0.756	0.167	4.815	17.143
	2	0.01	1.403	0.273	4.869	19.744
Mean		0.0924	1.2123	0.3709	4.9126	16.8437
M1		0.0326	0.0363	0.0484	0.0929	4.6603
M0		0.0155	0.0746	0.0504	0.0702	0.6476
F value		2.106	2.056	1.042	1.322	7.197
Signif.		NS	NS	NS	NS	*
Sw		0.125	0.273	0.225	0.265	0.805
Sb		0.093	0.000	0.000	0.106	1.416
St		0.155	0.273	0.225	0.286	1.629
Rel SD (St)		167.89%	22.54%	60.54%	5.81%	9.67%
F 0.05		1.88	1.83	1.79	1.83	2.1
Calc. F		0.0002	0.0007	0.0005	0.0008	0.0265
Est Degs F		9	10	11	10	6
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.820**			
Bias						
Uncertainty					± 25.17%	± 22.30%
Recovery					**113.54%**	**102.95%**
SD of Mean Recovery			13.47%		4.93%	9.32%
Se of Mean Recovery			4.063%		1.486%	2.811%

MBAA Limit of Detection = 0.820 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square

M_0 = Within Batch Mean Squares

sw = Within batch standard deviation

sb = Between batch standard deviation

st= Total standard deviation

NS - Not Significant

* - Significant at the 0.05 level

** - Significant at the 0.01 level

*** - Significant at the 0.001 level

Pass St not significantly larger than target

Table 2.6 Performance data of dichloroacetic acid (DCAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.14	1.558	1.388	5.922	16.363
	2	0.14	1.665	1.495	5.965	17.799
2	1	0.118	1.499	1.429	6.136	17.953
	2	0.117	1.435	1.395	6.185	17.87
3	1	0.01	1.317	1.349	5.879	17.948
	2	0.01	1.551	1.44	5.803	17.808
4	1	0.01	1.374	1.224	5.678	17.961
	2	0.01	1.53	1.306	5.75	17.606
5	1	0.01	0.986	1.363	5.948	17.848
	2	0.01	1.021	1.48	5.796	17.949
6	1	0.01	1.227	1.054	5.911	17.73
	2	0.01	1.16	1.112	5.845	17.75
Mean		0.0496	1.3603	1.3363	5.9015	17.7154
M1		0.0076	0.0974	0.0387	0.0436	0.2025
M0		0.0000	0.0084	0.0037	0.0036	0.1854
F value		91465.000	11.645	10.391	12.271	1.092
Signif.		***	***	***	***	NS
Sw		0.000	0.091	0.061	0.060	0.431
Sb		0.062	0.211	0.132	0.142	0.092
St		0.062	0.230	0.146	0.154	0.440
Rel SD (St)		124.51%	16.90%	10.90%	2.60%	2.49%
F 0.05		2.21	2.1	2.1	2.1	1.79
Calc. F		0.0000	0.0005	0.0002	0.0002	0.0019
Est Degs F		5	6	6	6	11
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.274**			
Bias						
Uncertainty					± 19.34%	± 7.34%
Recovery					**114.13%**	**102.37%**
SD of Mean Recovery			22.07%		2.77%	1.84%
Se of Mean Recovery			6.653%		0.835%	0.553%

DCAA Limit of Detection = 0.274 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square

M_0 = Within Batch Mean Squares

sw = Within batch standard deviation

sb = Between batch standard deviation

st= Total standard deviation

NS - Not Significant

* - Significant at the 0.05 level

** - Significant at the 0.01 level

*** - Significant at the 0.001 level

Pass St not significantly larger than target

Table 2.7 Performance data of bromochloroacetic acid (BCAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.083	1.556	3.306	7.041	16.164
	2	0.088	1.634	2.961	6.577	16.26
2	1	0.078	2.053	3.211	7.717	18.647
	2	0.068	2.111	3.376	7.048	19.099
3	1	0.01	1.078	2.751	5.624	14.934
	2	0.01	1.115	2.407	5.506	14.592
4	1	0.052	2.001	3.196	7.477	19.888
	2	0.045	1.955	3.209	7.255	18.878
5	1	0.01	2.251	3.572	9.484	25.088
	2	0.01	2.027	3.745	9.552	24.725
6	1	0.01	1.913	2.563	6.746	17.791
	2	0.01	1.945	2.72	6.544	19.569
Mean		0.0395	1.8033	3.0848	7.2143	18.8029
M1		0.0024	0.3119	0.3365	3.4268	24.2576
M0		0.0000	0.0053	0.0266	0.0643	0.3870
F value		163.586	58.352	12.645	53.301	62.686
Signif.		***	***	***	***	***
Sw		0.004	0.073	0.163	0.254	0.622
Sb		0.034	0.391	0.394	1.297	3.455
St		0.035	0.398	0.426	1.321	3.510
Rel SD (St)		87.45%	22.08%	13.81%	18.31%	18.67%
F 0.05		2.21	2.21	2.1	2.21	2.21
Calc. F		0.0000	0.0016	0.0018	0.0175	0.1232
Est Degs F		5	5	6	5	5
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.219**			
Bias						
Uncertainty					± 39.86%	± 39.10%
Recovery					**103.24%**	**98.24%**
SD of Mean Recovery			39.49%		18.48%	18.25%
Se of Mean Recovery			11.906%		5.571%	5.502%

BCAA Limit of Detection = 0.219 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square
M_0 = Within Batch Mean Squares
sw = Within batch standard deviation
sb = Between batch standard deviation
st= Total standard deviation

NS - Not Significant
* - Significant at the 0.05 level
** - Significant at the 0.01 level
*** - Significant at the 0.001 level
Pass St not significantly larger than target

Table 2.8 Performance data of dibromoacetic acid (DBAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.01	0.685	5.679	12.317	22.025
	2	0.01	0.907	4.635	9.132	21.107
2	1	0.052	2.416	5.453	11.99	24.482
	2	0.053	2.389	5.681	9.823	25.716
3	1	0.046	1.361	4.055	8.199	20.444
	2	0.047	1.343	4.447	8.607	17.197
4	1	0.01	2.022	4.21	11.221	28.411
	2	0.01	1.796	4.282	10.353	25.217
5	1	0	2.251	3.572	9.484	25.088
	2	0	2.027	7.554	9.552	24.725
6	1	0.053	2.251	3.745	8.634	21.314
	2	0.066	2.199	4.046	8.307	25.007
Mean		0.0298	1.8039	4.7799	9.8016	23.3944
M1		0.0013	0.7516	1.0888	2.7408	16.4816
M0		0.0000	0.0129	1.4373	1.3226	3.0733
F value		93.989	58.457	1.320	2.072	5.363
Signif.		***	***	NS	NS	**
Sw		0.004	0.113	1.199	1.150	1.753
Sb		0.026	0.608	0.000	0.842	2.589
St		0.026	0.618	1.199	1.425	3.127
Rel SD (St)		87.45%	34.27%	25.08%	14.54%	13.37%
F 0.05		2.21	2.21	1.79	1.88	2.01
Calc. F		0.0000	0.0038	0.0144	0.0203	0.0978
Est Degs F		5	5	11	9	7
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.340**			
Bias						
Uncertainty					± 54.63%	± 43.07%
Recovery					**125.54%**	**116.34%**
SD of Mean Recovery			61.30%		13.33%	13.81%
Se of Mean Recovery			18.484%		4.020%	4.165%

DBAA Limit of Detection = 0.340 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square
M_0 = Within Batch Mean Squares
sw = Within batch standard deviation
sb = Between batch standard deviation
st= Total standard deviation

NS - Not Significant
* - Significant at the 0.05 level
** - Significant at the 0.01 level
*** - Significant at the 0.001 level
Pass St not significantly larger than target

Table 2.9 Performance data of trichloroacetic acid (TCAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.01	0.983	0.259	4.577	16.074
	2	0.01	1.039	0.279	4.466	15.575
2	1	0.01	1.183	0.424	4.66	15.827
	2	0.01	1.149	0.385	4.552	15.972
3	1	0.01	1.182	0.61	4.203	14.368
	2	0.01	1.292	0.538	4.146	14.664
4	1	0.01	1.149	0.38	4.808	16.496
	2	0.01	1.151	0.407	4.653	16.817
5	1	0.01	1.202	0.486	4.774	16.292
	2	0.01	1.207	0.536	4.595	16.334
6	1	0.276	1.544	0.902	4.991	15.879
	2	0.243	1.524	0.874	4.922	15.935
Mean		0.0516	1.2171	0.5067	4.6123	15.8528
M1		0.0208	0.0602	0.0919	0.1350	1.0603
M0		0.0001	0.0014	0.0009	0.0073	0.0388
F value		228.651	42.967	99.168	18.402	27.328
Signif.		***	***	***	***	***
Sw		0.010	0.037	0.030	0.086	0.197
Sb		0.102	0.172	0.213	0.253	0.715
St		0.102	0.176	0.215	0.267	0.741
Rel SD (St)		197.89%	14.42%	42.52%	5.78%	4.68%
F 0.05		2.21	2.21	2.21	2.1	2.21
Calc. F		0.0001	0.0003	0.0005	0.0007	0.0055
Est Degs F		5	5	5	6	5
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.112**			
Bias						
Uncertainty					± 14.21%	± 13.44%
Recovery					**102.64%**	**95.91%**
SD of Mean Recovery			17.35%		5.77%	4.41%
Se of Mean Recovery			5.232%		1.738%	1.330%

TCAA Limit of Detection = 0.112 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square

M_0 = Within Batch Mean Squares

sw = Within batch standard deviation

sb = Between batch standard deviation

st= Total standard deviation

NS - Not Significant

* - Significant at the 0.05 level

** - Significant at the 0.01 level

*** - Significant at the 0.001 level

Pass St not significantly larger than target

Table 2.10 Performance data of bromodichloroacetic acid (BDCAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.01	0.45	0.523	3.86	19.951
	2	0.02	0.47	0.525	6.262	10.256
2	1	0.01	0.504	0.593	4.408	13.33
	2	0.01	0.403	0.728	4.212	12.29
3	1	0.01	0.369	0.782	5.345	14.071
	2	0.01	0.371	0.951	5.781	13.902
4	1	0.01	0.716	0.879	4.6	13.249
	2	0.01	0.681	0.88	4.523	13.391
5	1	0.01	0.793	1.024	4.901	13.627
	2	0.01	0.685	1.007	4.785	14.279
6	1	0.01	0.698	0.854	4.503	12.059
	2	0.01	0.701	0.842	4.094	11.661
Mean		0.0108	0.5701	0.7990	4.7728	13.5055
M1		0.0000	0.0510	0.0620	0.4785	2.4844
M0		0.0000	0.0020	0.0039	0.5154	7.9756
F value		1.000	26.042	15.767	1.077	3.210
Signif.		NS	***	***	NS	*
Sw		0.003	0.044	0.063	0.718	2.824
Sb		#NUM!	0.157	0.170	0.000	0.000
St		#NUM!	0.163	0.182	0.718	2.824
Rel SD (St)		0.00%	28.55%	22.73%	15.04%	20.91%
F 0.05		1.79	2.21	2.1	1.79	1.88
Calc. F		#NUM!	0.0003	0.0003	0.0052	0.0798
Est Degs F		11	5	6	11	9
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.133**			
Bias						
Uncertainty					± 30.74%	± 62.41%
Recovery					**99.35%**	**79.42%**
SD of Mean Recovery			15.97%		10.19%	6.63%
Se of Mean Recovery			4.815%		3.073%	2.000%

BDCAA Limit of Detection = 0.133 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square

M_0 = Within Batch Mean Squares

sw = Within batch standard deviation

sb = Between batch standard deviation

st= Total standard deviation

NS - Not Significant

* - Significant at the 0.05 level

** - Significant at the 0.01 level

*** - Significant at the 0.001 level

Pass St not significantly larger than target

Table 2.11 Performance data of chlorodibromoacetic acid (CDBAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.01	0.431	0.198	3.31	9.886
	2	0.01	0.433	0.3	3.136	10.143
2	1	0.01	0.67	0.334	3.741	11.333
	2	0.01	0.666	0.397	3.674	10.805
3	1	0.01	0.693	0.88	5.248	13.63
	2	0.01	0.682	0.77	5.818	13.255
4	1	0.01	0.44	0.655	4.24	12.332
	2	0.01	0.42	0.804	4.161	11.893
5	1	0.01	0.473	0.703	4.491	12.105
	2	0.01	0.473	0.81	4.228	12.531
6	1	0.01	0.435	0.681	3.994	10.859
	2	0.01	0.434	0.731	3.864	10.588
Mean		0.0100	0.5208	0.6053	4.1588	11.6133
M1		0.0000	0.0301	0.1125	1.2251	3.0944
M0		0.0000	0.0000	0.0052	0.0377	0.0778
F value		999.000	667.035	21.550	32.525	39.795
Signif.		***	***	***	***	***
Sw		0.000	0.007	0.072	0.194	0.279
Sb		0.000	0.123	0.232	0.771	1.228
St		0.000	0.123	0.243	0.795	1.259
Rel SD (St)		0.00%	23.58%	40.08%	19.11%	10.84%
F 0.05		0	2.21	2.21	2.21	2.21
Calc. F		0.0000	0.0002	0.0006	0.0063	0.0159
Est Degs F		0	5	5	5	5
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.020**			
Bias						
Uncertainty					± 49.38%	± 52.89%
Recovery					**88.84%**	**68.80%**
SD of Mean Recovery			12.27%		16.99%	7.49%
Se of Mean Recovery			3.701%		5.124%	2.259%

CDBAA Limit of Detection = 0.020 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square
M_0 = Within Batch Mean Squares
sw = Within batch standard deviation
sb = Between batch standard deviation
st= Total standard deviation

NS - Not Significant
* - Significant at the 0.05 level
** - Significant at the 0.01 level
*** - Significant at the 0.001 level
Pass St not significantly larger than target

Table 2.12 Performance data of tribromoacetic acid (TBAA)

Batch	Replicate	Concentration ng/L				
		DI Blank	LOD Sample	Tap Blank	Low Spike	High Spike
1	1	0.01	0.606	0.01	3.257	9.188
	2	0.01	0.589	0.01	2.55	9.632
2	1	0.01	0.565	0.01	3.62	11.816
	2	0.01	0.555	0.02	3.423	11.369
3	1	0.01	0.688	0.02	4.603	14.631
	2	0.01	0.639	0.01	5.693	13.827
4	1	0.01	0.679	0.01	3.772	11.987
	2	0.01	0.674	0.02	3.533	12.029
5	1	0.01	0.704	0.02	3.811	11.886
	2	0.01	0.68	0.02	3.735	12.175
6	1	0.01	0.611	0.01	3.124	10.131
	2	0.01	0.647	0.01	3.087	9.873
Mean		0.0100	0.6364	0.0142	3.6840	11.5453
M1		0.0000	0.0051	0.0000	1.2490	5.8381
M0		0.0000	0.0004	0.0000	0.1493	0.0996
F value		999.000	13.148	1.133	8.368	58.615
Signif.		***	**	NS	*	***
Sw		0.000	0.020	0.005	0.386	0.316
Sb		0.000	0.049	0.001	0.742	1.694
St		0.000	0.053	0.005	0.836	1.723
Rel SD (St)		0.00%	8.26%	36.45%	22.70%	14.92%
F 0.05		0	2.1	1.79	2.1	2.21
Calc. F		0.0000	0.0000	0.0000	0.0070	0.0297
Est Degs F		0	6	11	6	5
OK ?		****	Pass	Pass	Pass	Pass
L.O.D			**0.059**			
Bias						
Uncertainty					± 53.65%	± 57.78%
Recovery					**91.75%**	**72.07%**
SD of Mean Recovery			5.07%		19.69%	10.67%
Se of Mean Recovery			1.528%		5.936%	3.217%
90% CI of recovery			2.77%		10.76%	5.83%

TBAA Limit of Detection = 0.059 ug/L calculated using 3 x Sw

Where

M_1 = Between Batch Mean Square
M_0 = Within Batch Mean Squares
sw = Within batch standard deviation
sb = Between batch standard deviation
st= Total standard deviation

NS - Not Significant
* - Significant at the 0.05 level
** - Significant at the 0.01 level
*** - Significant at the 0.001 level
Pass St not significantly larger than target

2.4 Conclusion

An analytical method has been developed and validated to determine nine HAAs in final drinking water.

3. Survey of Final Drinking Water Leaving Water Treatment Works

As part of their contract with Defra, Cranfield University carried out a literature review on HAA levels in the UK, and liaised with the water companies to select and arrange access to appropriate sampling sites and locations for the sampling survey.

The survey was designed to target sites where conditions and treatment are considered conducive to the formation of HAAs. Treatment works sourcing surface water from both upland reservoirs and lowland rivers were monitored together with treatment works taking water from groundwater that are of higher risk of HAA formation such as those with high TOC. Drinking water which has undergone a wide range of treatment were monitored, including ozone and GAC as well as more conventional methods of filtration and purification.

Chloramination has been shown to lead to lower HAA formation and sites having this treatment were monitored. At present, only approximately 13% of UK treatment works use chloramination but they treat about 25% of the volume supplied. However, in the USA, chloramination has increased considerably to aid water companies in meeting the standard for a total of five HAAs and this might be anticipated in the UK should an EU standard for HAAs be introduced.

Following on from the initial survey carried out by Cranfield University, further sampling was carried out by both Cranfield and WRc, working in co-operation, of drinking water from 20 sites covering England and Wales. Overall, the 20 sites were sampled at least once in four separate surveys to give a preliminary indication of any variation with season.

3.1 Analysis

3.1.1 Gas Chromatography (GC)-µECD (Cranfield University)

This method and the results of the work carried out by Cranfield University are the subject of a separate report to DWI.

3.1.2 IC-MS/MS (STL)

Analysis of the site survey samples was carried out at STL's R&D Laboratory in Reading using the equipment dedicated for IC-MS/MS and carried out in accordance with the methodology developed in Section 2.

4. Survey Sites

For the monitoring of HAAs, 20 sites in England and Wales for sampling were agreed with DWI. These sites included lowland and upland surface waters and groundwater sources.

Target sites were selected where conditions and treatment existed which were likely to form HAAs as well as a range of raw water types and treatment processes. Therefore, these sites included surface waters from upland reservoirs and lowland rivers as well as groundwaters with a higher risk of HAA formation, for example, those with high TOC. Treatment processes included ozone, GAC and more conventional filtration and also site where chloramination was in use as this process is thought to reduce HAA formation.

The geographical distribution of the sites chosen is shown in Figure 4.1.

Figure 4.1 Geographical Distribution of the 20 Survey Sites

4.1 Other relevant data

WRc has experience in collecting relevant information on the source waters, water treatment procedures and prevailing geological conditions from water company staff at treatment works

or via the water quality managers. This information was gathered and collated during the surveys, together with further information supplied by Cranfield University, for which we are grateful.

Table 4.1 shows the drinking water treatment works sampled in this survey together with information on the treatment processes used and comments on any particular specific circumstances governing the treatment used on the site.

Table 4.1 HAA Survey Site Characteristics

Site	Source and Treatment	Comment
A	Upland reservoir. Aluminium sulphate coagulant, DAF clarifier, rapid gravity filtration (sand) primary filtration. On-site electrolytic chlorine disinfection.	High organic content, moorland fed reservoir water, low bromide, low alkalinity
B	Groundwater and surface water from 2 impounding reservoirs. Surface water is blended, groundwater is aerated then blended with surface water. Reservoir storage, coagulation (PACl), DAF, RGF, chlorination (Mn removal), RGF, sodium hydroxide for pH correction dosed before secondary filters. Orthophosphoric acid also dosed pre contact tank. Electrolytic chlorination, Sodium bisulphite used for trimming chlorine.	Reservoir with algal issues
C	Upland river abstraction, aluminium sulphate coagulant, floc blanket clarifier, rapid gravity primary filtration, chlorine gas disinfection.	Effluent impacted river, high organic content, low bromide
D	Borehole-fed, primary filtration adsorber (arsenic removal).	High bromide borehole water (control site)
E	Reservoir, coagulation (Fe, poly), FBC or DAF, RGF (anthracite/sand), GAC (F200, F400, 208A, EBCT 15 min), chlorination.	High bromide, lowland river
F	Direct river abstraction, pre-ozonation, coagulation (ferric and poly), floc blanket clarification, RGF (ASG), ozonation, GAC (F400, 30 min EBCT), chloramination.	Effluent impacted river
G	Lowland river abstraction, 20 rapid gravity filters, Actiflow clarifier, 12 GAC adsorbers, ozone interstage treatment, sodium hypochlorite disinfection.	Lowland river, just above bromide threshold
H	Upland reservoir. Microstrainer pretreatment, microfiltration primary treatment.	Pristine lake, some algal issues, low bromide
I	Upland reservoir, Feripol XL coagulant, DAF clarifier. Rapid gravity primary filtration. Secondary filtration manganese removal. Electrolytic chlorination.	Very high organic content

Site	Source and Treatment	Comment
J	Alum coagulation and DAF. Rapid gravity sand filtration. GAC adsorption. Super chlorination with gas Cl_2 followed by SO_2. Alkali pH correction with sodium hydroxide.	Particular blue-green algae issues
K	Reservoir, pre-ozonation, coagulation (ferric and poly), floc blanket clarification, RGF (ASG, 5 m/h), ozonation, GAC (TL830, 15 min EBCT), chlorination.	River supplied , algal impacted reservoir with high bromide, high alkalinity
L	Supplied from upland reservoir. Ferric coagulant (Ferripol XL, now ICL 12.5% ferric sulphate). Clarification through Centrifloc clarifiers and DAF. pH increase for manganese oxidation prior to filtration through RGFs. Lime for pH correction and ortho- phosphoric acid addition prior to disinfection with chlorine gas. A small supply to Mickleton and Bowes is then ammoniated for stable chloramines in the network.	Direct comparison of chlorination and chloramination possible, upland reservoir, low bromide
M	Reservoir, coagulation (Fe), DAF, RGF (ASG), GAC (F400, EBCT 14 min), chlorination.	Reservoir with recalcitrant organics
N	Confined groundwater from on-site boreholes, iron/manganese removal, chlorination using chlorine gas.	Borehole water (control site)
O	Upland reservoir, ozone pretreatment, aluminium sulphate coagulant.	Upland river, low bromide
P	Lowland reservoir. Primary filters, GAC, slow sand filtration, aeration to increase dissolved oxygen (DO) following degradation in slow sand stage, chlorination using chlorine gas, followed by ammonium sulphate addition to produce chloramine.	Reservoir, natural catchment, no coagulation
Q	Borehole abstraction. Aeration & potassium permanganate dosing. Before contact tank for iron and Mn removal, micro filtration, super chlorination. Dechlorination, then pumped to network and stored for approximately 4/5 days before gravitating into network.	Borehole water, high organic content but low colour, low bromide
R	Raw water pre-chlorination. Alum coagulation and dissolved air flotation (not clarifier). Rapid gravity filtration with GAC. Alkali pH correction with sodium carbonate. Super chlorination with gas Cl_2 followed by SO_2. Phosphoric acid dosing for plumbo-solvency.	Reservoir: pre-chlorination, general algae issues
S	Upland reservoir, ozone pre-treatment, aluminium sulphate coagulant, rapid gravity primary filtration, chlorine gas disinfection.	Lake, organic rich, at bromide threshold
T	Receives water from Site T impounding reservoir only,	Reservoir with algal

Site	Source and Treatment	Comment
	coagulation (PACl & poly), clarifiers, chlorination (Mn removal on filters), RGF, GAC, disinfection (sodium hypochlorite – bulk storage). Sodium hydroxide and orthophosphoric acid also dosed post contact tank. Sodium bisulphite used for trimming chlorine.	issues

Abbreviations:

ASG Anthracite/sand/garnet multi-media bed
AS Anthracite/sand dual media bed
DAF Dissolved Air Filtration
EBCT Empty Bed Contact Time
FBC Flat Bottomed Clarifier
GAC Granulated Activated Carbon
PACl Polyaluminium Chloride
RGF Rapid Gravity Filtration
SSF Slow Sand Filtration
VTF Vertical Flow Tank

5. Monitoring

5.1 Chlorinated samples

Samples of the final water were taken from the regulatory sampling point at each site. The sample tap was allowed to run for not less than 5 minutes before taking the sample. The sample was poured directly into glass bottles (60 mL) prepared specifically for sampling. These bottles contained a quenching agent (ammonium chloride) to prevent any further reaction with free chlorine. For each sample the bottle was filled completely to exclude as much air as possible. The filling was carried out gently and slowly taking care not to rinse out the quenching agent.

During each round of the sampling survey, in addition to the final water samples, several field blank samples were also taken. These were samples of pure deionized water held in glass bottles which were gently transferred to sample bottles containing the quenching agent at the location of the final water sample point.

Samples were labelled to identify the works and the date of sampling. The temperature of the sample was measured using a calibrated mercury in glass thermometer.

The samples were kept in the dark in cool-boxes containing frozen ice-packs at between approximately 4°C to 8°C during transit, and either taken directly to the analysing laboratory, or kept overnight in a cold-room at approximately 4°C until submission to the analysing laboratory within approximately 48 hours of sampling.

5.1.1 Sampling Survey 1

The first sampling survey was carried out in October 2009 by Cranfield University alone to provide samples for Gas Chromatography (GC)-µECD analysis. No samples were taken during this round for analysis using the IC-MS/MS method. This survey will not be considered further in this report.

5.1.2 Sampling Survey 2

Sampling survey 2 was carried out between 20th and 28th January 2010. Cranfield University sampled sites A, C, D, E, G, H, I, K, L, M, N, O, P, Q, and S. WRc sampled sites B, J and T. It was not possible to obtain samples from either Site R or Site F as these sites were not operating during the dates on which sampling was carried out. The samples were analysed within 7 to 14 days after sampling i.e. within the 14 day stability time determined in method development by the US EPA.

5.1.3 Sampling Survey 3

Sampling survey 3 was carried out between 26th April and 7th May 2010. Cranfield University sampled sites A, C, D, E, F, G, H, I, K, L, M, N, O, P, Q, and S. WRc sampled sites B, J, R and T. Unfortunately, problems with the serviceability of the analytical instrumentation at STL meant that the samples were not analysed until 26th May 2010. Thus the time between the samples being taken on site and actual analysis was between 19 and 28 days.

To determine the effect of the additional delay (beyond the 14 day storage time specified in the US EPA 557 method) a series of stability tests were undertaken using spiked water samples which were analysed at 21 days.

5.1.4 Sampling Survey 4

Sampling survey 4 was carried out between 19th July and 28th July 2010. Cranfield University sampled sites A, C, D, E, F, G, H, I, K, L, M, N, O, P, Q, and S. WRc sampled sites B, J, R and T. Once again analysis of the samples was delayed by failures in operation of the methodology resulting in AQC failures. As a result, final analysis was only confirmed on 28th August: a delay of between 30 and 37 days between the samples being taken and actual analysis.

5.1.5 Sampling Survey 5

To understand further the potential for changes in the samples analysed after the 14 day period recommended in the method (US EPA 557), additional sampling was carried out by STL between 23th December 2010 and 14th January 2011. The samples for this round were collected by water company staff and analysed in 1 to 15 days. This sampling round provided samples for long-term stability trials (day 0 to day 68) and also further results to add to the dataset on HAA levels analysed by this method. The results of this sampling session (Survey 5 are presented in Table 6.5). This round of sampling is incomplete due to operational changes at the treatment works sites and difficulties in organising the collection of samples. The results obtained can, however, be used with the results of earlier surveys to obtain a more complete 'picture' of the HAA concentrations detected using this new method. As the result of these further problems delaying the analysis, stability testing on samples of low and medium HAA concentrations (Site D below LOD and sites E and M with total HAA concentrations of 15-16 µg/L) were tested after 68 days storage at 4^{o}C. The results of these tests are shown in Appendix A Stability Tests (Tables A.9 to A.11). The results of the Stability Tests indicate that the samples are stable for up to 68 days analysed by this method. Nevertheless it may be prudent to interpret the results from Surveys 3 and 4 with some caution.

During Survey 5, spiked samples provided by RTC's analytical quality control scheme (RT-Corporation, Laramie, USA) were analysed for HAAs (only 6 HAAs were present in the test samples) and the results are shown in Table A.12. The results were within the range of certified values for all 6 HAAs.

6. Results

6.1 HAA Survey Results

For Surveys 3, 4 and 5 the time between sampling and analysis exceeded that recommended by US EPA for this method (US EPA 557). Although STL carried out a number of stability tests indicating that the samples were stable for up to 68 days, it may be prudent to treat these results with some caution.

The results obtained for the 9 individual HAAs and the total HAAs are given in Tables 6.2-6.5 and in Figures 6.1 and 6.2. In no case did the concentrations of the total HAAs detected exceed either the US standard for 5 HAAs of 60 µg/L or the value of 80 µg/L suggested for 9 HAA in the report of the review of the Drinking Water Directive. The World Health Organization (WHO) have set guideline values for three HAAs; monochloroacetic acid (20 µg/L), dichloroacetic acid (50 µg/L) and trichloroacetic acid (200 µg/L). None of the concentrations for these three HAAs measured in the four surveys exceeded the individual WHO values.

In general, the upland sites had higher levels of HAAs and some of these sites had been further identified as having higher organics. Among the sites having higher concentrations of HAAs, two, (Site F and Site P) have chloramination as part of their water treatment.

Taking into account Surveys 2, 3 and 4, the sites having higher levels of HAAs generally showed seasonal variation with HAAs being at their lowest in the winter (Survey 2, limited data suggest water temperatures of approximately 5-8^{o}C) and increasing to peak in summer (Survey 4, water temperatures 10-21^{o}C) (Figure 6.2). Survey 5 taken over a period from December 2010 to January 2011 gave results higher than those detected in the previous winter period. The two borehole sites (Site D and Site N) which could be considered as controls, both had low levels of HAAs. As no water temperatures were taken for samples in Survey 5, there are no data on any differences in the conditions in the two winter periods. The samples for Survey 2 were taken from the 20th to 28th January 2010 when the weather was cold with some snow and Survey 5 was undertaken between 23rd December 2010 and 14th January 2011 which coincided, in general with the end of a cold period and the start of warmer weather. Dichloroacetic acid (DCA) and trichloroacetic acid (TCA) are the most common HAAs detected with DCA seen at higher levels than TCA. This is in agreement with other surveys on HAAs in drinking water including that conducted in the UK by Parsons *et al*. (2009). The maximum concentration of DCA detected was 26.3 µg/L and TCA, 14.5 µg/L.

The next most commonly seen HAA was bromochloroacetic acid. The bromoacetic acids were seen only at low concentration, if at all. Table 6.1 shows the mean and standard deviation (SD) for DCA, TCA and total HAAs. There was a wide range in the levels of these

chemicals but in general, the concentrations detected were similar to those seen in other surveys including Parsons *et al*., (2009).

A number of sampling sites have been identified as having low or high bromide levels (see Table 4.1). However, there did not appear to be a correlation between high bromide levels and high HAAs or high brominated HAAs or vice versa. However, many other factors may negate any effects of bromide, for example site D has high bromide levels but being fed from a borehole, is considered to be a control site and has low HAAs.

Table 6.1 Mean concentrations of DCA, TCA and Total HAAs (µg/L)

Survey Round		DCA	TCA	Total HAA
2	Mean	4.21	2.92	9.80
	SD	2.24	1.79	5.92
	N	16	14	18
3	Mean	4.45	3.12	13.75
	SD	3.29	2.02	7.08
	N	20	20	20
4	Mean	7.10	3.97	19.54
	SD	6.78	3.94	13.51
	N	18	20	20
5	Mean	5.51	4.98	16.05
	SD	3.34	3.11	10.50
	N	11	11	12

Table 6.2 Round 2 HAA Survey Results (IC-MS/MS method) (all values as µg/L)

Site	Sampled	Analysed	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA	HAA9
Site A	25/01/2010	04/02/2010	0.5	<0.8	6.9	1.1	4.9	<0.4	0.5	<0.2	<0.2	13.9
Site B	26/01/2010	04/02/2010	0.6	<0.8	7.3	5.3	3.5	1.8	2.1	0.8	<0.2	21.4
Site C	27/01/2010	04/02/2010	<0.2	<0.8	0.8	0.6	0.3	<0.4	0.2	<0.2	<0.2	1.9
Site D	20/01/2010	04/02/2010	<0.2	<0.8	<0.3	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2	<lod
Site E	20/01/2010	04/02/2010	0.4	<0.8	3.6	2.7	2.7	1.2	2.3	0.9	<0.2	13.8
Site F	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site G	25/01/2010	04/02/2010	0.2	<0.8	1.9	1.7	<0.2	1.1	0.6	0.5	<0.2	6
Site H	26/01/2010	04/02/2010	0.8	<0.8	8.6	1.3	7.3	<0.4	0.9	<0.2	<0.2	18.9
Site I	25/01/2010	04/02/2010	0.5	<0.8	6.2	2	3.7	<0.4	0.7	<0.2	<0.2	13.1
Site J	20/01/2010	04/02/2010	0.2	<0.8	2.6	1.4	1.4	<0.4	1	0.4	<0.2	7
Site K	28/01/2010	04/02/2010	<0.2	<0.8	1.4	2.6	<0.2	4.2	0.5	1.1	0.7	10.5
Site L	27/01/2010	04/02/2010	0.4	<0.8	5.9	0.7	4	<0.4	0.4	<0.2	<0.2	11.4
Site M	20/01/2010	04/02/2010	0.4	<0.8	4.5	2.9	2.2	1.1	1.9	0.6	<0.2	13.6
Site N	28/01/2010	04/02/2010	<0.2	<0.8	<0.3	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2	<lod
Site O	26/01/2010	04/02/2010	0.2	<0.8	2.5	1	1.3	<0.4	0.5	<0.2	<0.2	5.5
Site P	28/01/2010	04/02/2010	0.5	<0.8	4.3	2.3	2.3	0.6	1.4	0.3	<0.2	11.7
Site Q	27/01/2010	04/02/2010	0.3	<0.8	3.8	1.9	3.8	0.5	1.8	0.4	<0.2	12.5
Site R	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site S	26/01/2010	04/02/2010	0.2	<0.8	3.2	0.9	2	<0.4	0.5	<0.2	<0.2	6.8
Site T	26/01/2010	04/02/2010	0.4	<0.8	3.9	1.5	1.5	0.5	0.5	0.1	<0.2	8.4

Table 6.3 Round 3 HAA Survey Results (IC-MS/MS method) (all values as µg/L)

Site	Sampled	Analysed	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA	HAA9
Site A	04/05/2010	26/05/2010	1.6	0.8	11.2	2.0	5.5	0.1	0.4	<0.2	<0.2	21.5
Site B	26/04/2010	26/05/2010	1.9	1.7	7.7	5.9	5.2	2.6	2.6	0.3	<0.2	27.8
Site C	06/05/2010	26/05/2010	0.6	0.8	1.0	0.7	1.0	<0.4	<0.2	<0.2	<0.2	4.1
Site D	28/04/2010	26/05/2010	0.5	0.9	0.3	<0.2	0.7	<0.4	<0.2	<0.2	<0.2	2.4
Site E	28/04/2010	26/05/2010	1.0	1.4	1.8	2.0	1.6	1.2	1.4	1.0	<0.2	11.3
Site F	07/05/2010	26/05/2010	1.5	1.1	2.0	2.6	1.2	2.3	1.1	0.9	<0.2	12.5
Site G	30/04/2010	26/05/2010	1.0	0.9	0.7	0.9	0.8	1.5	<0.2	<0.2	<0.2	5.7
Site H	05/05/2010	26/05/2010	1.3	0.9	9.3	1.3	7.1	<0.4	1.2	<0.2	<0.2	21.0
Site I	30/04/2010	26/05/2010	1.9	<0.8	9.3	2.3	5.1	<0.4	0.8	<0.2	<0.2	19.4
Site J	28/04/2010	26/05/2010	1.2	1.2	4.2	2.9	3.1	1.1	1.6	<0.2	<0.2	15.2
Site K	07/05/2010	26/05/2010	1.1	1.5	1.5	2.6	0.9	4.3	0.5	1.6	0.8	14.9
Site L	06/05/2010	26/05/2010	0.8	<0.8	6.2	0.7	5.1	<0.4	0.5	<0.2	<0.2	13.2
Site M	28/04/2010	26/05/2010	1.0	1.3	5.0	2.6	3.0	0.5	2.1	0.2	<0.2	15.6
Site N	07/05/2010	26/05/2010	0.4	0.9	0.3	<0.2	0.8	<0.4	<0.2	<0.2	<0.2	2.4
Site O	05/05/2010	26/05/2010	0.8	1.0	3.1	1.1	1.8	<0.4	0.5	<0.2	<0.2	8.3
Site P	07/05/2010	26/05/2010	0.7	0.9	3.8	2.3	2.8	0.6	2.1	<0.2	<0.2	13.1
Site Q	06/05/2010	26/05/2010	1.5	1.0	3.3	1.9	3.3	0.7	1.9	<0.2	<0.2	13.7
Site R	28/04/2010	26/05/2010	1.6	1.7	6.6	3.2	5.9	1.3	2.0	<0.2	<0.2	22.3
Site S	05/05/2010	26/05/2010	0.5	<0.8	4.4	0.8	2.9	<0.4	0.6	<0.2	<0.2	9.2
Site T	26/04/2010	26/05/2010	1.4	1.1	7.5	3.5	4.6	1.7	1.6	<0.2	<0.2	21.3

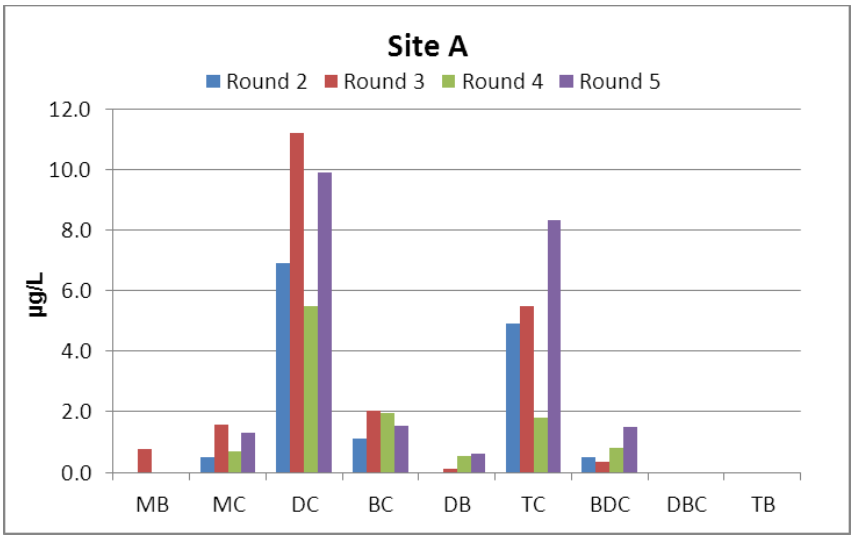
Table 6.4 Round 4 HAA Survey Results (IC-MS/MS method) (all values as µg/L)

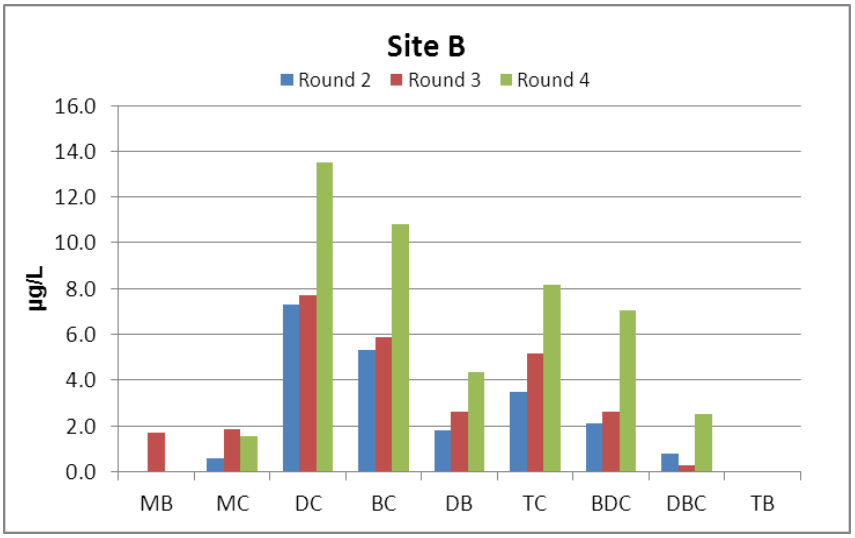
Site	Sampled	Analysed	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA	HAA9
Site A	26/07/2010	29/08/2010	0.7	<0.8	5.5	2.0	1.8	0.5	0.8	<0.2	<0.2	11.2
Site B	27/07/2010	29/08/2010	1.5	<0.8	13.5	10.8	8.2	4.4	7.1	2.5	<0.2	48.0
Site C	28/07/2010	29/08/2010	<0.2	<0.8	3.0	1.4	1.9	0.4	1.1	<0.2	<0.2	7.7
Site D	19/07/2010	29/08/2010	<0.2	<0.8	<0.3	<0.2	0.3	<0.4	<0.2	<0.2	<0.2	0.3
Site E	19/07/2010	29/08/2010	0.5	<0.8	3.1	5.3	2.7	3.4	5.5	4.4	0.7	25.6
Site F	21/07/2010	29/08/2010	0.3	<0.8	2.6	5.1	1.4	5.3	2.5	3.5	1.4	22.1
Site G	26/07/2010	29/08/2010	<0.2	<0.8	0.7	1.7	0.3	2.2	0.5	1.0	0.1	6.5
Site H	27/07/2010	29/08/2010	2.3	<0.8	26.3	3.3	14.5	0.2	2.1	<0.2	<0.2	48.6
Site I	26/07/2010	29/08/2010	0.7	<0.8	5.3	2.6	2.6	1.2	1.5	<0.2	<0.2	13.8
Site J	27/07/2010	29/08/2010	<0.2	<0.8	1.3	2.2	0.8	2.1	1.6	1.2	<0.2	9.2
Site K	21/07/2010	29/08/2010	<0.2	<0.8	1.6	4.2	0.9	5.3	1.6	3.5	1.9	19.0
Site L	28/07/2010	29/08/2010	1.6	<0.8	19.8	1.6	12.4	<0.4	1.4	<0.2	<0.2	36.8
Site M	19/07/2010	29/08/2010	0.2	<0.8	4.3	5.0	2.8	2.1	4.0	2.3	<0.2	20.6
Site N	21/07/2010	29/08/2010	<0.2	<0.8	<0.3	<0.2	0.3	<0.4	<0.2	<0.2	<0.2	0.3
Site O	27/07/2010	29/08/2010	0.5	<0.8	8.8	2.4	4.7	0.4	1.7	<0.2	<0.2	18.4
Site P	21/07/2010	29/08/2010	0.9	<0.8	8.5	4.9	5.8	1.2	5.1	1.5	<0.2	27.8
Site Q	28/07/2010	29/08/2010	0.3	<0.8	3.8	3.1	4.9	1.5	3.7	1.1	<0.2	18.4
Site R	27/07/2010	29/08/2010	1.0	<0.8	9.9	4.5	6.5	1.4	3.9	0.8	<0.2	28.0
Site S	27/07/2010	29/08/2010	0.5	<0.8	6.7	2.1	4.8	0.3	1.9	<0.2	<0.2	16.4
Site T	27/07/2010	29/08/2010	0.2	<0.8	3.1	2.5	2.1	1.8	1.7	0.7	<0.2	12.1

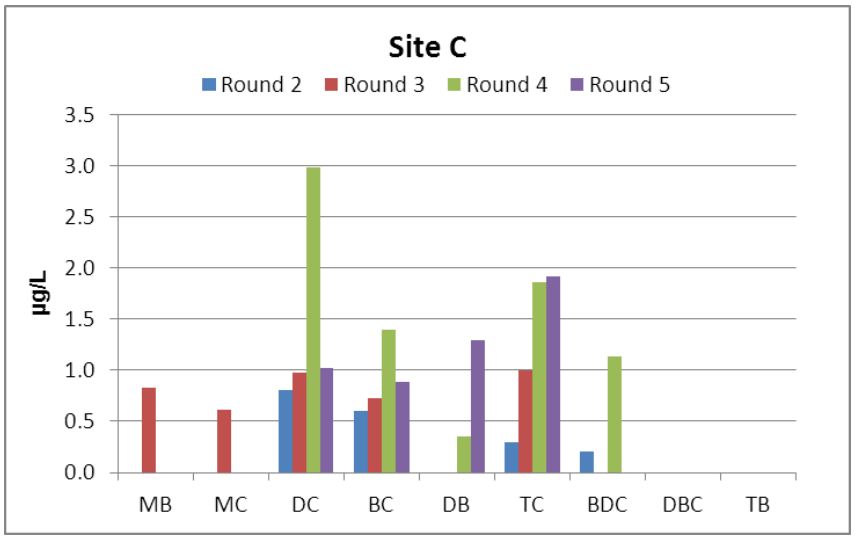
Table 6.5 Round 5 HAA Survey Results (IC-MS/MS method) (all values as µg/L)

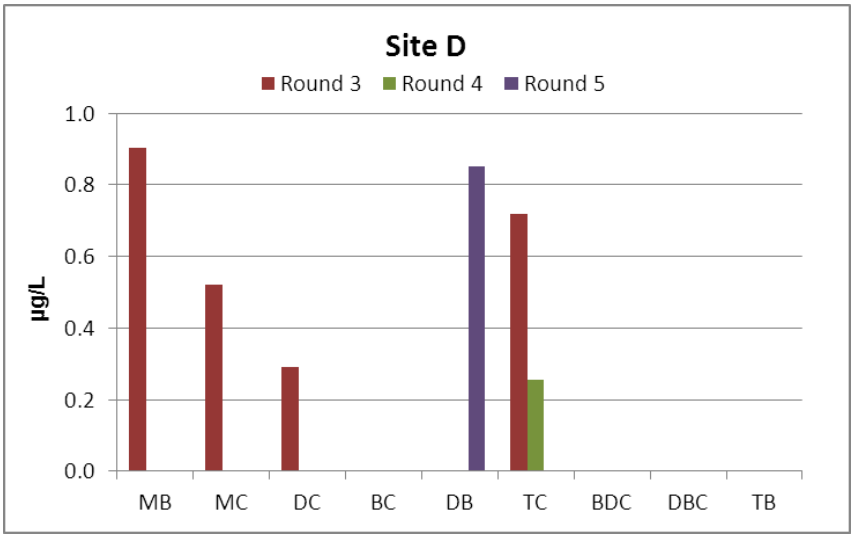
Site	Sampled	Analysed	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA	HAA9
Site A	29/12/2010	07/01/2011	1.3	<0.8	9.9	1.5	8.3	0.6	1.5	<0.2	<0.2	23.1
Site B	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site C	29/12/2010	07/01/2011	<0.2	<0.8	1.0	0.9	1.9	0.4	1.1	<0.2	<0.2	5.3
Site D	29/12/2010	07/01/2011	<0.2	<0.8	<0.3	<0.2	0.2	0.9	<0.2	<0.2	<0.2	1.1
Site E	29/12/2010	07/01/2011	<0.2	<0.8	2.6	3.1	3.7	2.2	1.8	0.5	<0.2	13.9
Site F	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site G	29/12/2010	07/01/2011	1.2	<0.8	2.1	2.4	1.8	2.1	0.4	<0.2	<0.2	10.0
Site H	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site I	23/12/2010	07/01/2011	<0.2	<0.8	5.4	2.0	3.9	0.9	1.0	<0.2	<0.2	13.2
Site J	14/01/2011	17/01/2011	<0.2	<0.8	2.9	3.2	1.5	<0.4	0.5	<0.2	<0.2	8.1
Site K	06/01/2011	07/01/2011	<0.2	<0.8	8.5	9.8	6.0	9.6	<0.2	<0.2	<0.2	33.9
Site L	29/12/2010	07/01/2011	<0.2	<0.8	5.2	0.7	4.5	0.5	0.6	<0.2	<0.2	11.5
Site M	29/12/2010	07/01/2011	<0.2	<0.8	3.9	4.0	4.0	2.3	1.1	<0.2	<0.2	15.3
Site N	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site O	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site P	06/01/2011	07/01/2011	<0.2	<0.8	9.1	8.6	7.9	6.0	1.2	<0.2	<0.2	32.8
Site Q	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site R	14/01/2011	17/01/2011	<0.2	<0.8	10.0	3.2	11.3	<0.4	0.3	<0.2	<0.2	24.8
Site S	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns
Site T	not sampled	not sampled	ns	ns	ns	ns	ns	ns	ns	ns	ns	ns

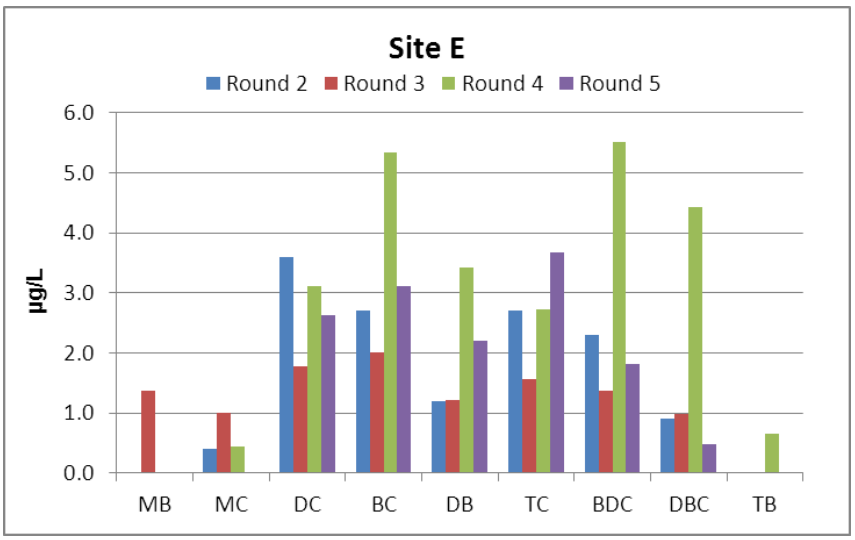
Figure 6.1 Plots showing concentrations of individual HAAs at each site

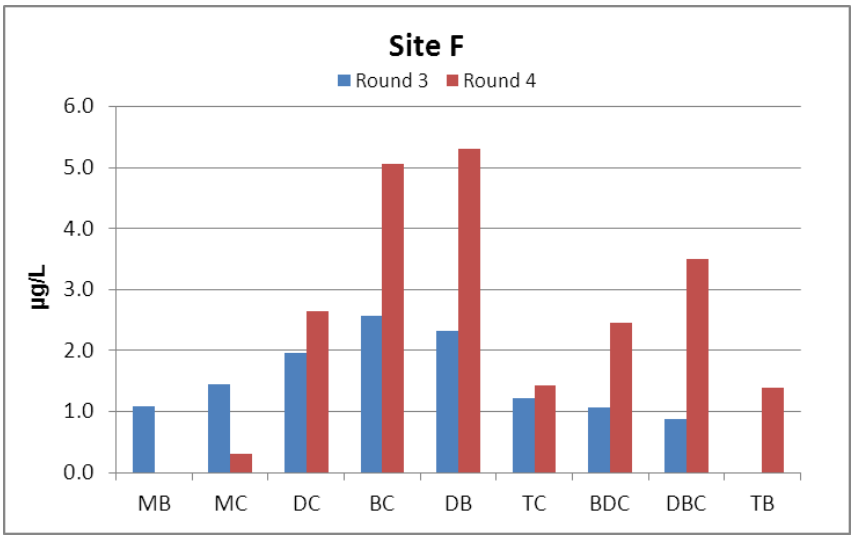


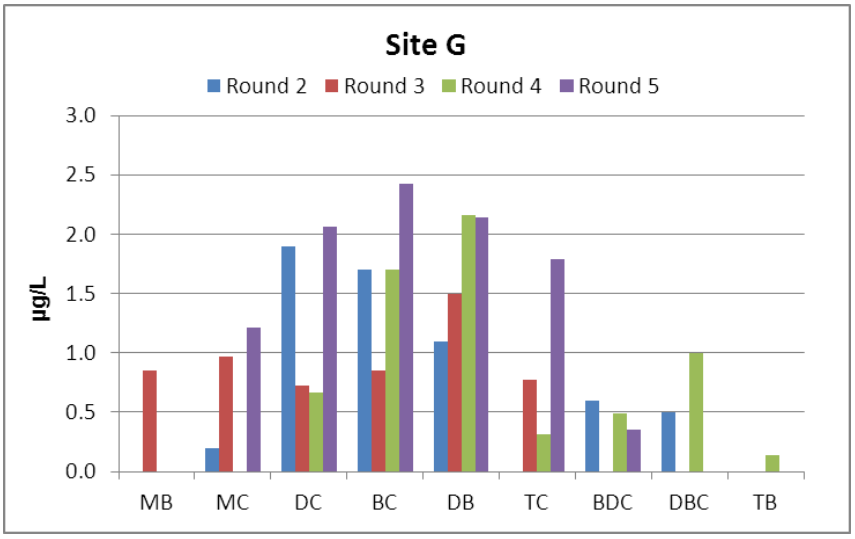


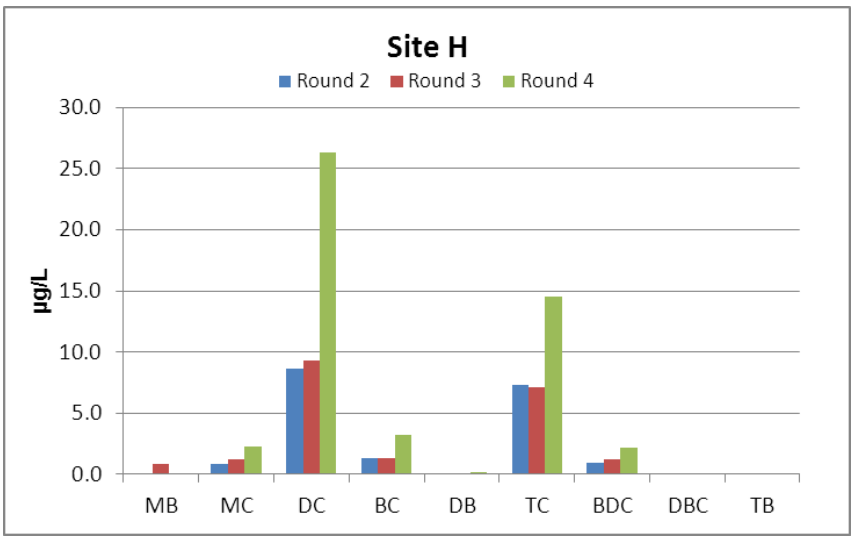

Site C
Round 2
Round 3
Round 4
Round 5
µg/L
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

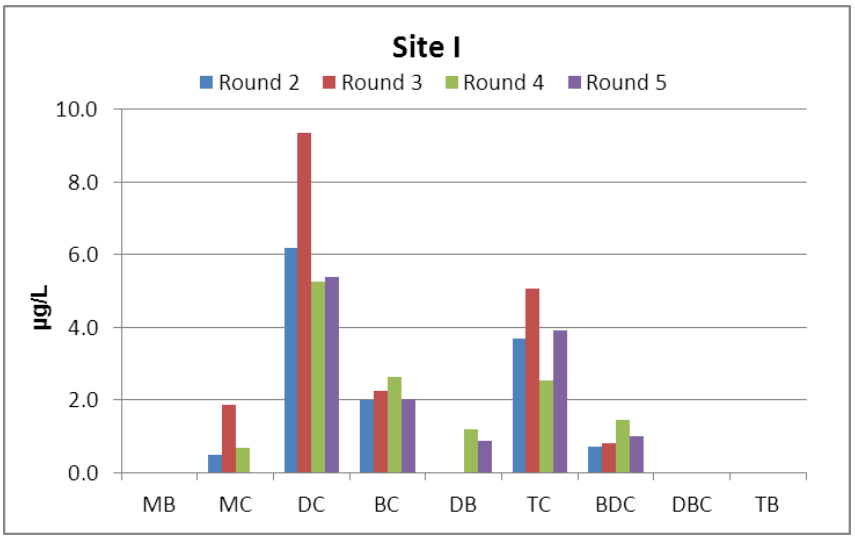

Site D
Round 3
Round 4
Round 5
µg/L
1.0
0.8
0.6
0.4
0.2
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

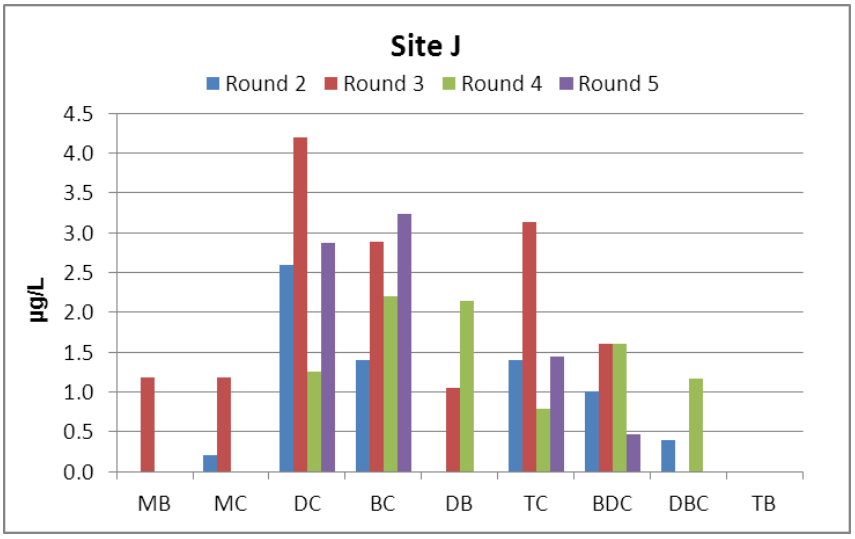

Site E
Round 2
Round 3
Round 4
Round 5
µg/L
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

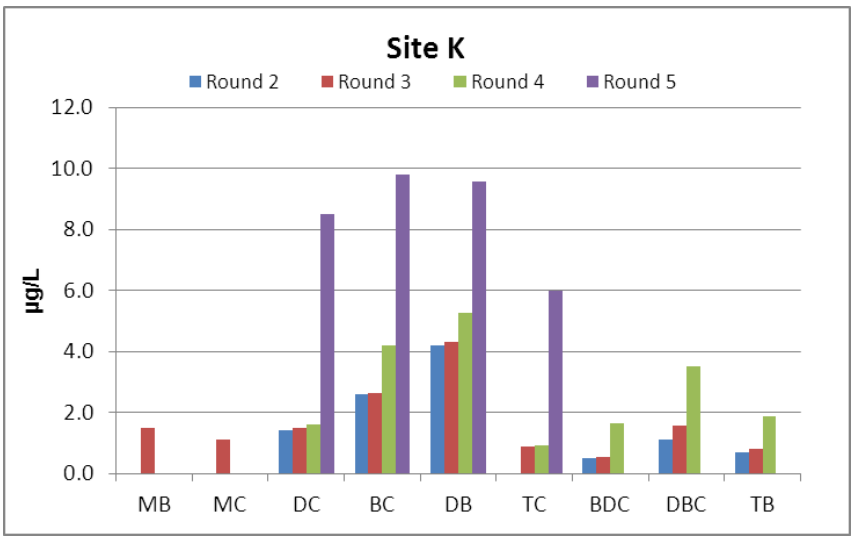

Site F
Round 3
Round 4
6.0
5.0
4.0
3.0
2.0
1.0
0.0
µg/L
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

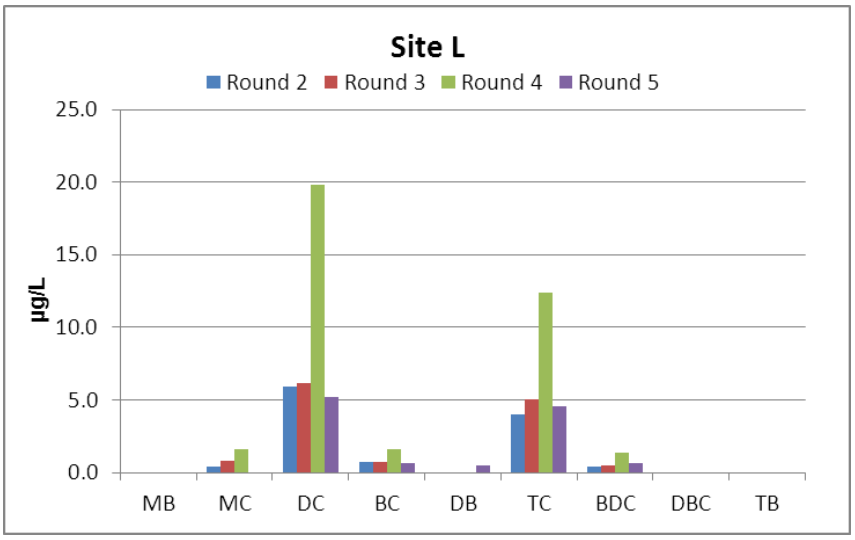

Site G
Round 2
Round 3
Round 4
Round 5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
µg/L
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

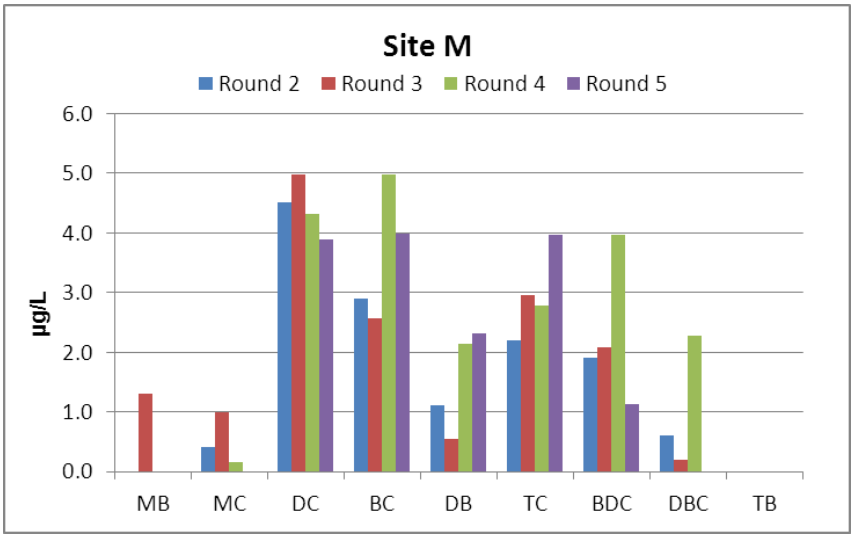

Site H
Round 2
Round 3
Round 4
30.0
25.0
20.0
15.0
10.0
5.0
0.0
µg/L
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

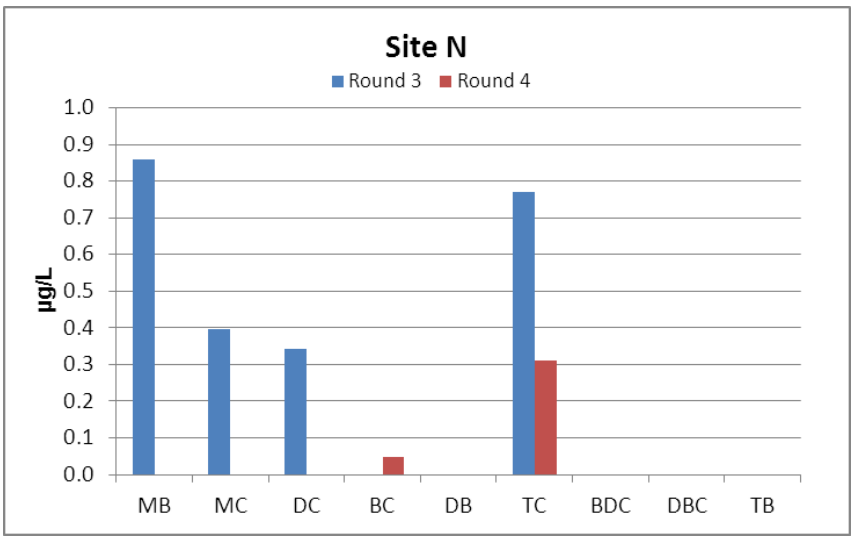

Site I
Round 2
Round 3
Round 4
Round 5
µg/L
10.0
8.0
6.0
4.0
2.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

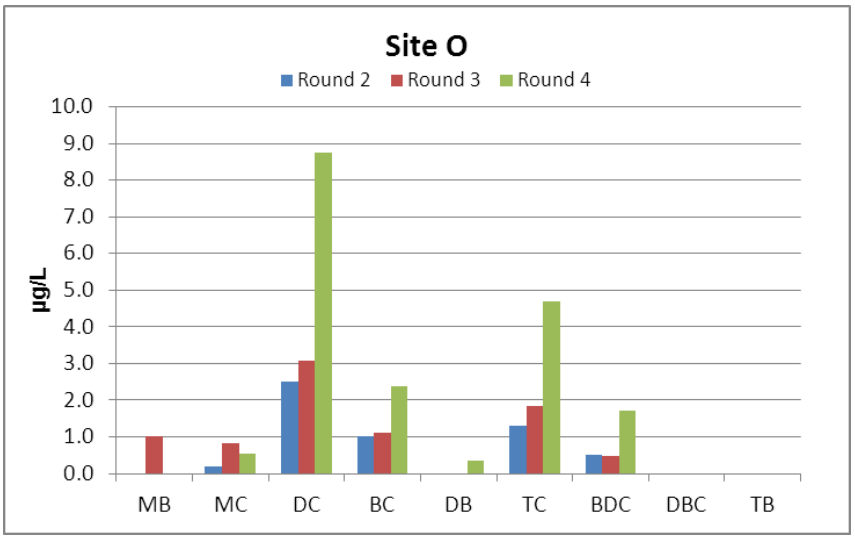

Site J
Round 2
Round 3
Round 4
Round 5
µg/L
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

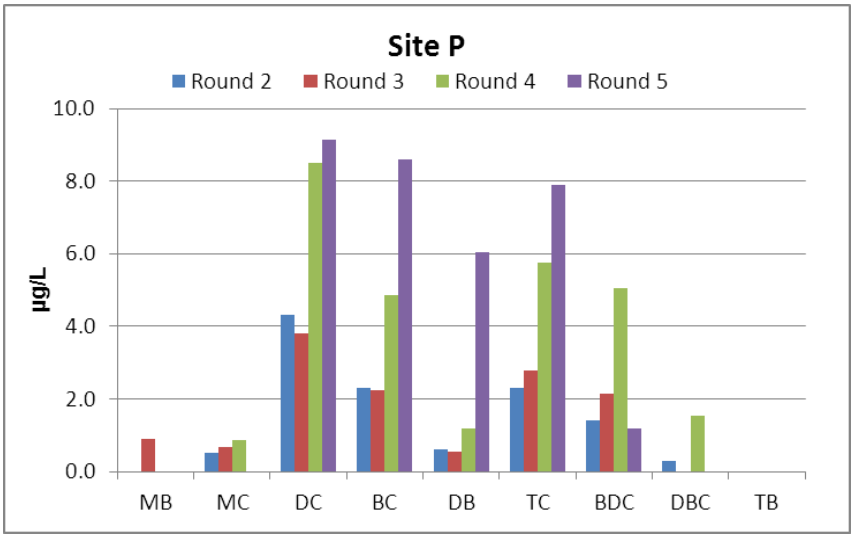

Site K
Round 2
Round 3
Round 4
Round 5
µg/L
12.0
10.0
8.0
6.0
4.0
2.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

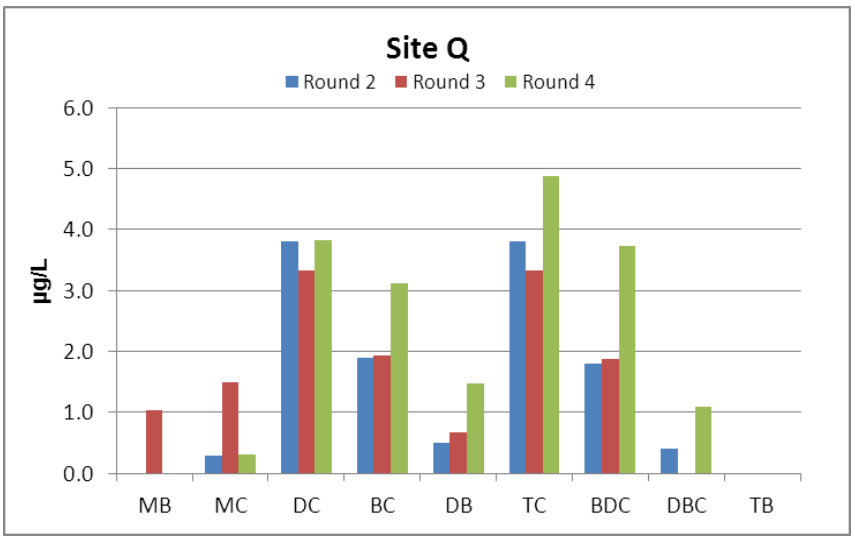

Site L
Round 2
Round 3
Round 4
Round 5
25.0
20.0
15.0
10.0
5.0
0.0
µg/L
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

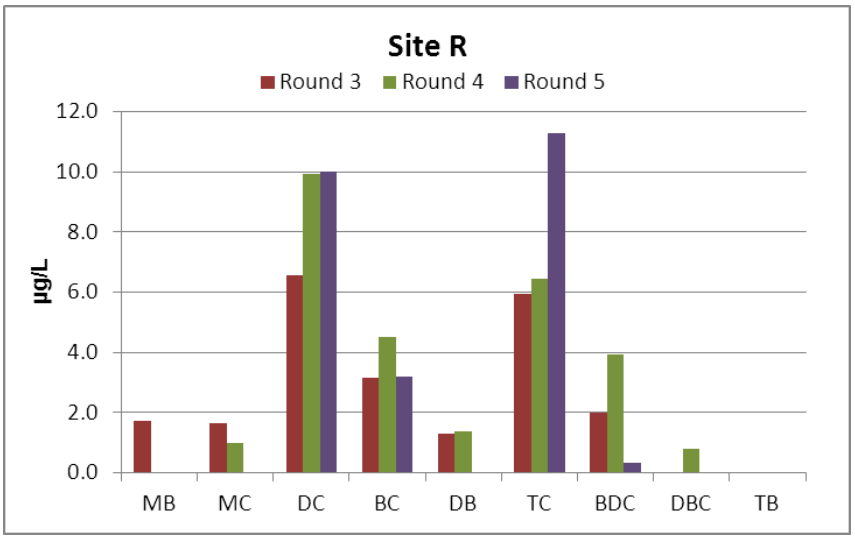

Site M
Round 2
Round 3
Round 4
Round 5
6.0
5.0
4.0
3.0
2.0
1.0
0.0
µg/L
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

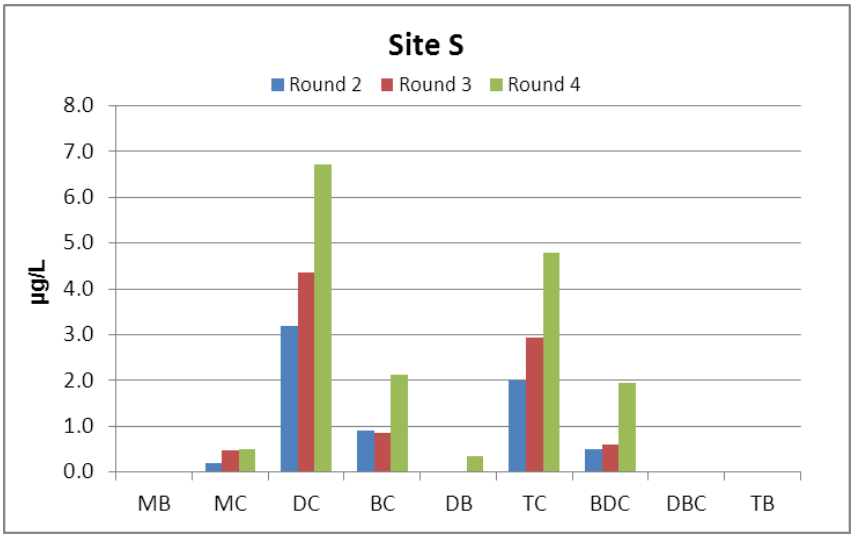

Site N
Round 3
Round 4
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
µg/L
MB
MC
DC
BC
DB
TC
BDC
DBC
TB


Site O
Round 2
Round 3
Round 4
µg/L
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB


Site P
Round 2
Round 3
Round 4
Round 5
µg/L
10.0
8.0
6.0
4.0
2.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB


Site Q
Round 2
Round 3
Round 4
µg/L
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB


Site R
Round 3
Round 4
Round 5
µg/L
12.0
10.0
8.0
6.0
4.0
2.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB


Site S
Round 2
Round 3
Round 4
µg/L
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

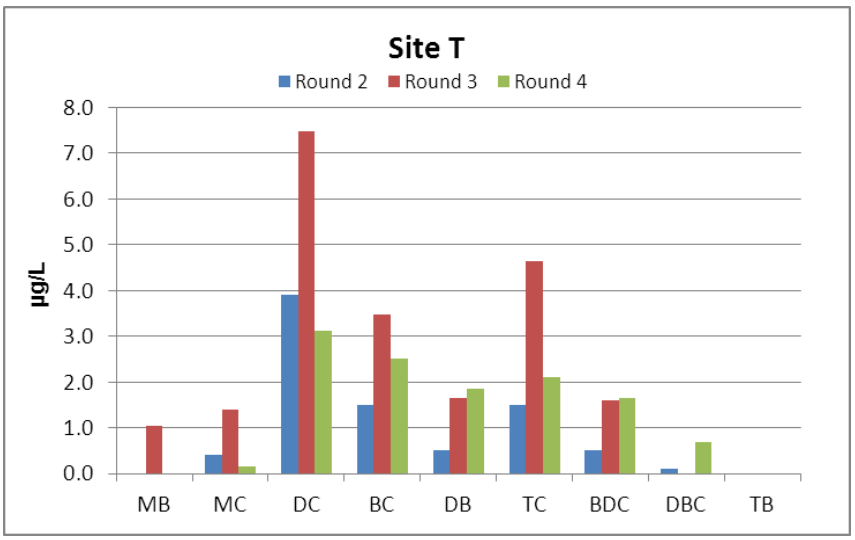
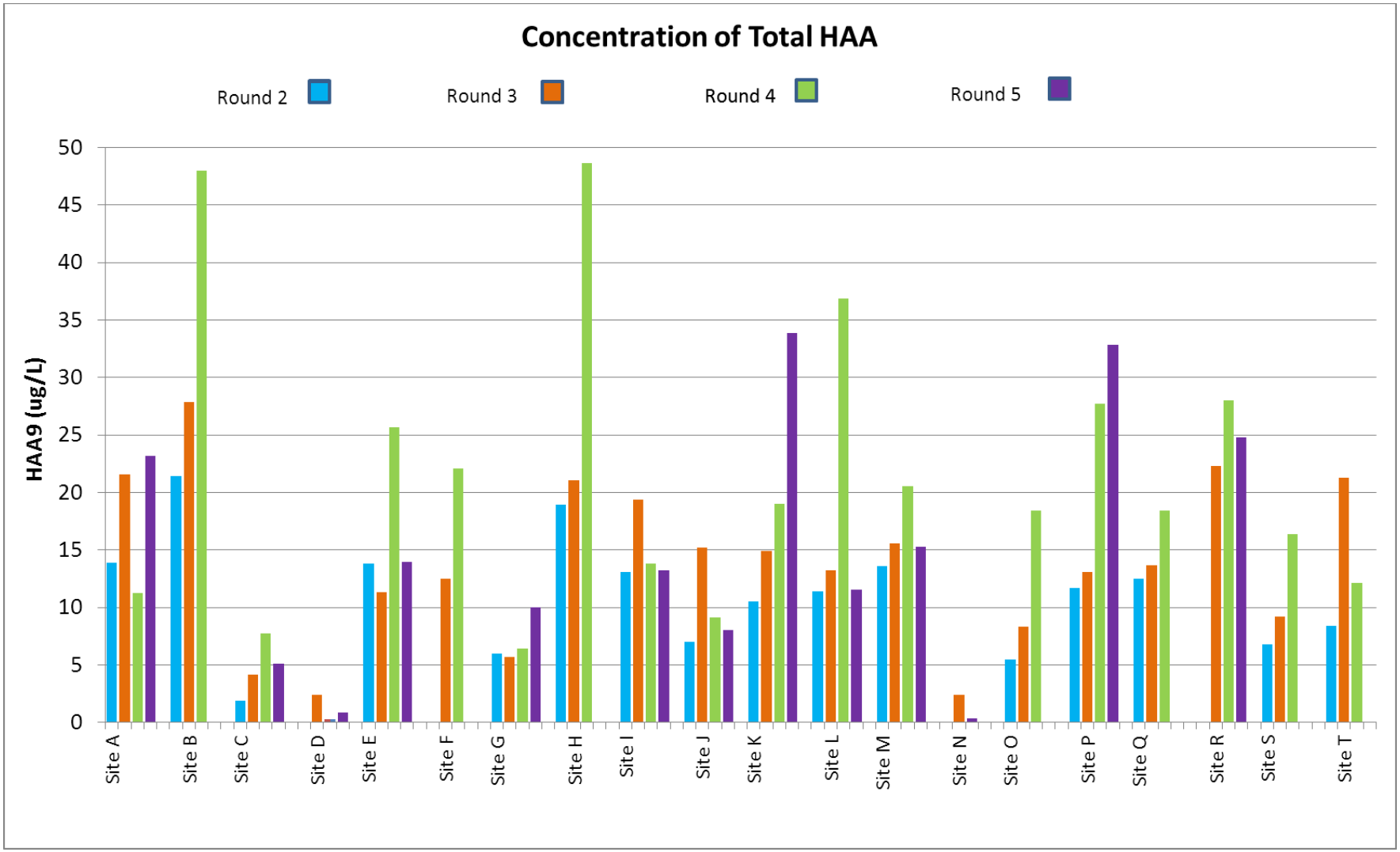

Site T
Round 2
Round 3
Round 4
µg/L
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
MB
MC
DC
BC
DB
TC
BDC
DBC
TB

Figure 6.2 Plot showing concentrations of total HAAs in each survey



7. Possible Implications for Water Supplies

At present there is no standard or parameter set for HAAs in the UK, while in the USA there is a standard of 60 µg/L for 5 HAAs. The recent review of potential revisions to the European Drinking Water Directive suggested that a parameter value of 80 µg/L for a total of 9 HAAs should be considered if they were identified by a Drinking Water Safety Plan or needed to be controlled by product specification. It has recently been decided that the DWD will not be revised with effort being concentrated to the improved monitoring of small supplies and the development of risk assessment and management through Drinking Water Safety Plans.

Before this project, the data on concentrations of HAAs in UK waters were limited. The monitoring conducted by Cranfield University using the original methodology on waters from 20 sites over 4 different seasonal periods will greatly add to the knowledge of HAAs in the UK.

The monitoring carried out by WRc and STL will add to these data but also introduced into the UK, the recently developed analytical method. This method, when fully validated should, as it is by direct injection without extraction or derivitisation, prove a more rapid, robust and cheaper method to run although the initial outlay on equipment may be considerable. Such a method would be useful if widespread monitoring of HAAs became routine in the UK. In the USA, there is routine monitoring using the original method but the new method was developed there in a response to the need for a more rapid and robust method. To complete the validation exercise necessary for this methodology, further monitoring would be required with multiple monitoring at a few sites to prove accuracy and precision statistically.

Section 5 describes delays between sampling and analysis for two of the sampling rounds and the further work done to obtain greater confidence in the results. Section 6 presents the results that were obtained and the conclusions in this section are based on accepting the analysed results based on the conducted stability test to 68 days, although samples taken in Surveys 3 and 4 were analysed after the US EPA stability limit of 14 days. All the monitoring results obtained in this survey of water leaving treatment works gave total HAAs of significantly less than 80 µg/L, the potential parameter value for 9 HAAs. In addition the survey included a number of sites which incorporate significant risk factors for HAA formation. Even if HAA concentrations rise within the distribution system, it seems unlikely that 80 µg/L will be exceeded at customers' taps.

Generally in the USA and to a certain much lower extent in the UK, the inability to maintain low levels of THMs and HAAs has led to an increased use of chloramination which appears to lower their levels. However, there is some evidence that chloramination may give rise to higher levels of other DBPs. A reduction in the levels of organic material in the water may lead to a reduction in THMs and HAAs. In this project, the two sites that were identified as using chloramination had higher levels of HAAs, although, of course, the concentration of HAAs detected before chloramination had not been determined.

The concentrations of HAAs seen in this survey using the new method gave similar results to that seen in other monitoring of drinking water including that conducted recently in the UK (Parsons *et al*., 2009). The results seen in the UK recently (contrary to the monitoring described by Malliarou *et al*., 2005) do not indicate that raised HAAs levels are a problem in the UK.

8. Conclusions and Recommendations

The project represents the first use in the UK of the recently developed IC-MS/MS method for the detection of HAAs. This method proved rapid and the samples appear stable over a long period of time although there were some technical difficulties in the methodology that prevented full compliance with the EPA recommended maximum storage times for the method. The results of the sampling surveys gave results similar to those described in other surveys conducted including others in the UK. For the complete validation of this method, it is recommended that multiple samples are collected from a few sites at regular intervals (e.g. monthly). This would enable the collation of statistically valid data for measuring the accuracy and precision of the new method.

This method is likely to be increasingly used for the measurement of HAAs as it is rapid, sensitive and potentially cheaper (after the initial outlay on equipment) than the existing methods based on GC which requires extraction and derivitisation. In parallel to this method development and its first use to detect HAAs at 20 sites, Cranfield University have been conducting a full seasonal survey of the same HAAs at the same sites. A full comparison of the concentrations detected by each method from samples taken at the same time is an important step and a unique opportunity in the potential use of the new method, and a chance to uncover any potential problems in its routine use.

The results of samples from 20 water treatment works in England indicate that the total HAAs concentrations are below those set as standard in the USA for 5 HAAs and the value suggested in the report of the review of the EU DWD for the 9 HAAs. In sites with higher levels of HAAs there is a tendency for seasonal variation with the lowest results being in the winter months with levels then increasing towards and peaking in summer. Higher levels were detected in samples from upland sites including those identified as having higher organic content.

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Blake, S., Hall, T., Harman, M., Kanda, R., McLaughlin, C.M., and Rumsby, P.C. (2009) Perchlorate – Risks to UK drinking water sources. Drinking water Inspectorate, Defra 7845 9DWI170/2/218), March 2009.

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US Environmental Protection Agency (1998). National Primary Drinking Water Regulations: Disinfectants and Disinfection Byproducts, Federal Register: December 16, 1998 (Volume 63, Number 241).

US EPA 552.3 (2003) Determination of haloacetic acids and dalapon in drinking water by liquid-liquid microextraction, derivatization, and gas chromatography with electron capture detection.

US Environmental Protection Agency (2006). National Primary Drinking Water Regulations: Stage 2 Disinfectants and Disinfection Byproducts Rule; Final Rule, 40 CFR Parts 9, 141, and 142.

US EPA Method 557 (2009). Determination of haloacetic acids, bromate and dalapon in drinking water by ion chromatography electrospray ionization tandem mass spectrometry (IC/ESI-MS/MS).

Appendix A Stability Tests

The results of the stability tests, field and laboratory blanks and the 'spiking' trials are shown in Tables A.1-A.12.

During method development, stability tests on spiked laboratory deionized water were completed to 21 days (Table A.1). The results for individual HAAs showed some small but statistically significant differences, but generally, the stability was considered to be satisfactory for the method.

Further trials were conducted spiking field blanks from a number of sites (with 2 µg/l of each HAA; Tables A.2 and A.3) and laboratory deionized water (with10 µg/l of each HAA; Tables A.4 and A.5). Although again there was some variability, this was considered acceptable for the method.

In Survey 3, samples from all sites were spiked with 2 µg/l of each HAA and the results are shown in Tables A.6 and A.7). In Table A.8, the results were analysed as follows to give a percentage recovery: Spiked sample – Sample ÷ 2 x 100 (for samples <LOD, 0.5 LOD was taken). Again the results for individual HAAs, in general, showed some small variability but the recoveries for the majority of the sites were satisfactory. There were also some larger anomalies which were more difficult to explain with several recoveries as low as 24% and one site, B, having several low recoveries.

However, problems in completing the analysis of the samples promptly owing to technical difficulties meant that a further stability test to 68 days was conducted using actual samples from 3 sites which had low or medium levels of HAAs (Table A.11). Both of these tests showed satisfactory stability. The results of the other validation tests were also satisfactory.

During sampling in Survey 5, samples provided by RTC analytical quality control scheme were analysed for 6 HAAs together with further spiked laboratory deionized water samples (10, 10, 5, 2, 1 and 0.5 µg/l) and the results are shown in Table A12. The results were within the range of certified values for all 6 HAAs.

In general, the results of the stability and recovery tests were considered satisfactory for a new method. However, for the complete validation of this method, it is recommended that multiple samples are collected from a few sites at regular intervals (e.g. monthly). This would enable the collation of statistically valid data for measuring the accuracy and precision of the new method.

Table A. 1 HAA Stability Test Results (Laboratory Water) 21 days stability at 5º C (all values as µg/L)

	MBAA		MCAA		DCAA		BCAA		DBAA		TCAA		BDCAA		CDBAA		TBAA	
	day 0	day 21	day 0	day 21	day 0	day 21	day 0	day 21	day 0	day 21	day 0	day 21	day 0	day 21	day 0	day 21	day 0	day 21
Sample 1	11.3	10.7	10.5	10.5	10.9	11.1	11.3	10.2	12.3	12.4	9.8	10.7	12.3	11.8	11.5	10.4	10.8	12.5
Sample 2	11.7	10.2	10.5	10.7	10.9	11.1	11.1	10.9	10.7	12.6	9.1	10.6	12.1	11.8	13.0	10.2	11.5	12.5
Sample 3	11.9	10.8	10.4	10.8	10.9	11.2	9.5	12.0	8.6	13.2	9.5	10.5	12.6	11.9	12.9	10.1	11.9	12.7
Sample 4	12.0	10.8	10.1	10.9	10.9	11.1	10.4	11.5	9.2	13.4	9.3	10.8	11.8	11.8	12.5	10.6	11.8	13.1
Sample 5	12.1	10.8	10.0	10.7	10.6	11.1	10.3	11.3	6.4	11.5	9.4	10.6	12.1	11.5	13.4	10.2	11.7	12.6
number	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0	5.0
Average	11.80	10.66	10.30	10.72	10.84	11.12	10.52	11.18	9.44	12.62	9.42	10.64	12.18	11.76	12.66	10.30	11.54	12.68
S.D.	0.32	0.26	0.23	0.15	0.13	0.04	0.71	0.68	2.22	0.75	0.27	0.11	0.29	0.15	0.72	0.20	0.44	0.25
pooled VAR	0.08		0.04		0.01		0.48		2.74		0.04		0.06		0.28		0.13	
Mean difference	1.14		0.42		0.28		0.66		3.18		1.22		-0.42		-2.36		1.14	
pooled sd	0.29		0.20		0.10		0.69		1.65		0.21		0.23		0.53		0.36	
mean diff%	-10		4		3		6		34		13		-3		-19		10	
Num SQRT	0.63		0.63		0.63		0.63		0.63		0.63		0.63		0.63		0.63	
sigma d	0.18		0.12		0.06		0.44		1.05		0.13		0.15		0.34		0.23	
t statistic	6.22		3.38		4.43		1.50		3.04		9.25		-2.83		-7.03		5.05	
t from tables	2.31		2.31		2.31		2.31		2.31		2.31		2.31		2.31		2.31	
Significance	SIG		SIG		SIG		NISG		SIG		SIG		SIG		SIG		SIG	
df	8.0		8.0		8.0		8.0		8.0		8.0		8.0		8.0		8.0	

Table A. 2 Spiking Trials – Field blanks (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Site A	0.52	0.78	<0.3	<0.2	0.54	<0.4	<0.2	<0.2	<0.2
Site B	1.29	1.74	1.14	1.01	1.81	0.87	<0.2	<0.2	<0.2
Site C	0.55	0.79	<0.3	<0.2	0.57	<0.4	<0.2	<0.2	<0.2
Site H	0.56	0.96	0.28	<0.2	0.63	<0.4	<0.2	<0.2	<0.2
Site J	0.79	0.99	0.61	0.43	0.87	0.38	<0.2	<0.2	<0.2
Site M	0.66	1.01	0.43	<0.2	0.90	<0.4	<0.2	<0.2	<0.2
Site T	0.82	1.16	0.70	0.45	1.14	0.46	<0.2	<0.2	<0.2

Table A. 3 Spiking Trials – Spiked field blanks (2 µg/L added) (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Site A	1.98	2.84	2.41	2.58	2.48	2.16	1.99	2.17	2.48
Site B	2.10	2.98	2.26	2.26	2.48	2.20	1.96	1.85	2.14
Site C	2.30	3.10	2.38	1.77	2.59	0.92	1.84	2.15	2.39
Site H	2.35	2.82	2.49	2.11	2.55	1.52	1.86	1.83	2.10
Site J	2.54	3.23	2.29	2.28	2.54	1.95	2.16	1.96	2.26
Site M	3.15	3.49	3.30	2.50	3.45	1.20	1.82	2.06	2.10
Site T	2.25	2.44	2.51	2.25	2.35	2.04	1.87	1.67	1.97

Table A. 4 Spiking Trials – Laboratory blanks (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Blank	<0.2	<0.8	<0.3	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2
Blank	<0.2	<0.8	<0.3	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2
Blank	<0.2	<0.8	<0.3	<0.2	<0.2	<0.4	<0.2	<0.2	<0.2

Table A. 5 Spiking Trials – Spiked laboratory blanks (10 µg/L added) (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Spike	10.50	11.30	11.10	11.30	9.83	12.30	12.30	11.50	10.80
Spike	10.10	12.00	10.90	11.50	9.34	9.15	11.80	12.50	11.80
Spike	11.30	12.20	10.90	10.40	9.66	6.54	12.70	13.20	12.40

Table A. 6 HAA Levels in Samples taken during spiking trials (Round 3) (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Site A	1.57	0.79	11.20	2.04	5.48	0.11	0.36	<0.2	<0.2
Site B	1.85	1.70	7.69	5.89	5.16	2.60	2.64	0.30	<0.2
Site C	0.61	0.83	0.98	0.73	0.99	<0.4	<0.2	<0.2	<0.2
Site D	0.52	0.90	0.29	<0.2	0.72	<0.4	<0.2	<0.2	<0.2
Site E	1.00	1.38	1.77	2.01	1.57	1.22	1.37	0.99	<0.2
Site F	1.45	1.08	1.96	2.56	1.21	2.32	1.06	0.88	<0.2
Site G	0.97	0.86	0.73	0.86	0.78	1.50	<0.2	<0.2	<0.2
Site H	1.26	0.86	9.31	1.30	7.10	<0.4	1.22	<0.2	<0.2
Site I	1.87	<0.8	9.34	2.25	5.08	<0.4	0.82	<0.2	<0.2
Site J	1.18	1.18	4.20	2.88	3.13	1.05	1.61	<0.2	<0.2
Site K	1.13	1.49	1.51	2.63	0.89	4.32	0.55	1.57	0.80
Site L	0.79	<0.8	6.15	0.74	5.07	<0.4	0.46	<0.2	<0.2
Site M	1.00	1.30	4.98	2.57	2.95	0.54	2.07	0.20	<0.2
Site N	0.40	0.86	0.34	<0.2	0.77	<0.4	<0.2	<0.2	<0.2
Site O	0.83	1.00	3.08	1.11	1.84	<0.4	0.49	<0.2	<0.2
Site P	0.68	0.89	3.81	2.25	2.77	0.56	2.14	<0.2	<0.2
Site Q	1.49	1.03	3.32	1.94	3.32	0.68	1.88	<0.2	<0.2
Site R	1.64	1.74	6.56	3.15	5.94	1.28	2.00	<0.2	<0.2
Site S	0.48	<0.8	4.35	0.85	2.94	<0.4	0.60	<0.2	<0.2
Site T	1.39	1.05	7.47	3.47	4.63	1.65	1.59	<0.2	<0.2

Table A. 7 HAA Levels in Spiked Samples (2 µg/L added) (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Site A	3.50	3.18	13.50	4.54	7.28	2.19	2.19	1.45	1.70
Site B	2.69	3.44	8.86	6.79	5.76	3.14	4.70	2.57	1.56
Site C	2.36	3.26	3.22	2.84	3.05	2.30	2.02	1.93	1.92
Site D	2.34	3.25	2.49	1.84	2.70	0.98	1.70	1.76	1.84
Site E	2.69	3.55	3.92	3.74	3.58	2.25	3.57	3.74	2.53
Site F	3.49	3.68	4.25	4.95	3.11	4.60	3.18	3.22	2.36
Site G	2.74	3.06	3.02	2.90	2.64	3.21	2.06	2.33	2.34
Site H	3.06	3.35	11.70	3.62	8.29	1.61	2.92	1.43	1.59
Site I	3.04	2.75	11.70	4.12	6.62	1.91	2.53	1.29	1.49
Site J	2.97	3.19	6.27	4.85	4.66	3.02	3.71	2.26	1.80
Site K	3.24	3.57	3.59	4.88	3.01	6.02	2.78	4.23	3.51
Site L	2.88	3.06	8.41	2.93	7.02	1.62	2.23	1.51	1.52
Site M	2.96	3.61	7.14	4.47	4.92	1.63	3.83	2.50	1.78
Site N	2.33	3.28	2.52	2.17	2.64	1.77	1.56	1.57	1.84
Site O	2.24	3.21	5.04	3.17	3.63	1.47	2.48	2.17	2.02
Site P	2.91	3.06	6.24	4.68	4.63	2.31	3.96	2.55	1.80
Site Q	2.79	3.42	5.90	4.13	5.10	2.43	3.95	2.40	1.76
Site R	2.98	3.41	7.89	4.71	6.42	2.97	3.79	1.80	1.46
Site S	2.92	2.92	6.53	2.92	4.41	1.47	2.47	1.59	1.68
Site T	2.90	3.01	8.75	5.17	6.19	3.32	3.74	1.93	1.65

Table A. 8 Percentage recovery of 2 µg/L HAA spike (all values as µg/L)

Sample Name	MCAA	MBAA	DCAA	BCAA	TCAA	DBAA	BDCAA	DBCAA	TBAA
Site A	96.5	119.5	115	125	90	104	91.5	67.5	80
Site B	42	87	58.5	45	30	27	103	113.5	73
Site C	87.5	121.5	112	105.5	103	105	96	91.5	91
Site D	91	117.5	110	87	99	39	80	83	87
Site E	84.5	108.5	107.5	86.5	100.5	51.5	110	137.5	121.5
Site F	102	130	114.5	119.5	95	114	106	117	113
Site G	88.5	110	114.5	102	93	85.5	98	111.5	112
Site H	90	124.5	119.5	116	59.5	70.5	85	66.5	74.5
Site I	58.5	117.5	118	93.5	77	85.5	85.5	59.5	69.5
Site J	89.5	100.5	103.5	98.5	76.5	98.5	105	108	85
Site K	105.5	104	104	112.5	106	85	111.5	133	135.5
Site L	104.5	133	113	109.5	97.5	71	88.5	70.5	71
Site M	98	115.5	108	95	98.5	54.5	88	115	84
Site N	96.5	121	109	103.5	93.5	78.5	73	73.5	87
Site O	70.5	110.5	98	103	89.5	63.5	99.5	103.5	96
Site P	111.5	108.5	121.5	121.5	93	87.5	91	122.5	85
Site Q	65	119.5	129	109.5	89	87.5	103.5	115	83
Site R	67	83.5	66.5	78	24	84.5	89.5	85	68
Site S	122	126	109	103.5	73.5	63.5	93.5	74.5	79
Site T	75.5	98	64	85	78	83.5	107.5	91.5	77.5

Table A. 9 HAA levels in tap water – Time = 0 days (all values as µg/L)

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Site E Replicate 1	0.00	0.31	3.35	2.83	1.93	2.97	3.01	1.28	0.00
Site E Replicate 2	0.00	0.14	3.24	2.96	1.84	2.80	3.41	1.34	0.00
Site E Replicate 3	0.00	0.23	3.29	2.90	1.79	2.31	3.08	1.25	0.00
Site E Replicate 4	0.00	0.18	3.31	3.13	2.03	2.48	3.41	1.48	0.00
Site E Replicate 5	0.47	0.00	3.11	3.38	1.98	2.69	3.12	1.59	0.00
Site E Replicate 6	0.45	0.18	3.14	3.43	2.08	2.62	3.34	1.82	0.00
Site E Replicate 7	0.54	0.32	3.14	3.28	2.00	2.23	3.21	1.45	0.00
Site E Replicate 8	0.25	0.47	3.19	3.29	1.95	2.56	3.13	1.83	0.00
Site E Replicate 9	0.73	0.00	3.17	3.20	1.95	3.18	4.37	2.67	0.00
Average	0.27	0.20	3.21	3.15	1.95	2.65	3.34	1.63	0.00
Site M Replicate 1	0.00	0.11	4.20	2.97	1.38	2.85	1.96	0.54	0.00
Site M Replicate 2	0.00	0.07	4.26	3.07	1.48	2.92	2.29	0.76	0.00
Site M Replicate 3	0.00	0.25	4.13	3.17	1.53	2.41	2.12	0.70	0.00
Site M Replicate 4	0.00	0.02	4.14	3.02	1.41	2.64	2.18	0.73	0.00
Site M Replicate 5	0.38	0.24	4.19	2.95	1.41	2.79	2.16	0.80	0.00
Site M Replicate 6	0.80	0.05	4.01	3.10	1.45	2.77	2.23	1.04	0.00
Site M Replicate 7	0.45	0.26	4.12	3.13	1.46	2.85	2.19	0.96	0.00
Site M Replicate 8	0.22	0.29	4.18	3.27	1.49	2.71	2.35	1.18	0.00
Site M Replicate 9	0.20	0.00	4.17	3.30	1.64	2.50	2.80	0.83	0.00
Average	0.23	0.14	4.15	3.11	1.47	2.71	2.25	0.83	0.00

Table A. 9 (cont.)

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Site D Replicate 1	0.00	0.00	0.19	0.09	0.31	0.00	0.00	0.00	0.00
Site D Replicate 2	0.00	0.00	0.18	0.09	0.33	0.00	0.00	0.00	0.00
Site D Replicate 3	0.00	0.06	0.18	0.10	0.32	0.00	0.00	0.00	0.00
Site D Replicate 4	0.00	0.00	0.18	0.09	0.30	0.00	0.00	0.00	0.00
Site D Replicate 5	0.39	0.00	0.20	0.09	0.33	0.00	0.00	0.00	0.00
Site D Replicate 6	0.11	0.00	0.19	0.10	0.33	0.00	0.00	0.00	0.00
Site D Replicate 7	0.45	0.00	0.19	0.09	0.32	0.00	0.00	0.00	0.00
Site D Replicate 8	0.18	0.00	0.19	0.09	0.31	0.00	0.00	0.00	0.00
Site D Replicate 9	0.18	0.00	0.19	0.09	0.31	0.00	0.00	0.00	0.00
Average	0.15	0.01	0.19	0.09	0.32	0.00	0.00	0.00	0.00

Table A. 10 HAA levels in tap water – stored at 4°C - Time = 68 days (all values as µg/L)

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Site E Replicate 1	0.00	0.00	3.48	3.89	2.55	2.89	2.54	1.16	0.00
Site E Replicate 2	0.07	0.59	3.68	3.63	2.53	3.31	2.26	1.05	0.00
Site E Replicate 3	0.00	0.37	3.23	3.69	2.59	3.08	2.46	1.16	0.00
Site E Replicate 4	0.17	0.54	3.05	3.91	2.51	3.27	2.33	1.06	0.00
Site E Replicate 5	0.00	0.00	3.18	3.53	2.30	2.81	2.27	1.01	0.00
Site E Replicate 6	0.20	0.00	3.48	3.68	2.65	3.04	2.13	0.87	0.00
Site E Replicate 7	0.09	0.41	2.97	3.41	2.34	2.34	2.01	0.97	0.00
Site E Replicate 8	0.06	0.19	3.41	3.65	2.72	3.34	2.12	1.02	0.00
Site E Replicate 9	0.00	0.76	3.31	3.47	1.93	3.91	2.02	0.82	0.00
Average	0.07	0.32	3.31	3.65	2.46	3.11	2.24	1.01	0.00
Site M Replicate 1	0.00	1.75	5.03	3.82	1.52	3.03	1.16	0.39	0.00
Site M Replicate 2	0.00	0.00	4.94	3.74	1.56	4.17	1.15	0.39	0.00
Site M Replicate 3	0.00	0.47	5.06	3.71	1.12	3.55	1.22	0.46	0.00
Site M Replicate 4	0.00	0.00	5.07	3.53	1.08	3.63	1.14	0.45	0.00
Site M Replicate 5	0.00	0.08	4.91	3.61	1.17	3.86	1.31	0.54	0.00
Site M Replicate 6	0.00	0.01	5.40	3.63	1.20	3.68	1.41	0.60	0.00
Site M Replicate 7	0.00	0.00	5.21	3.61	1.27	3.79	1.51	0.61	0.00
Site M Replicate 8	0.00	0.27	5.14	3.77	1.35	3.78	1.36	0.56	0.00
Site M Replicate 9	0.00	0.00	5.30	3.81	1.23	3.75	1.40	0.55	0.00
Average	0.00	0.29	5.12	3.69	1.28	3.69	1.30	0.50	0.00

Table A. 10 (cont.)

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Site D Replicate 1	0.00	0.21	0.40	0.06	0.10	0.00	0.00	0.00	0.00
Site D Replicate 2	0.00	0.00	0.36	0.01	0.08	0.00	0.00	0.00	0.00
Site D Replicate 3	0.00	0.00	0.20	0.00	0.03	0.00	0.00	0.00	0.00
Site D Replicate 4	0.00	0.00	0.09	0.00	0.04	0.00	0.00	0.00	0.00
Site D Replicate 5	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.00
Site D Replicate 6	0.00	0.00	0.25	0.00	0.02	0.00	0.00	0.00	0.00
Site D Replicate 7	0.00	0.00	0.19	0.00	0.06	0.00	0.00	0.00	0.00
Site D Replicate 8	0.00	0.00	0.19	0.05	0.15	0.00	0.00	0.00	0.00
Site D Replicate 9	0.00	0.00	0.21	0.00	0.06	0.00	0.00	0.00	0.00
Average	0.00	0.02	0.22	0.01	0.06	0.00	0.00	0.00	0.00

Table A. 11 HAA stability data summary (all values as µg/L)

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Site E									
Average T=0 Days	<0.8	0.20	3.21	3.15	1.95	2.65	3.34	1.63	<0.2
Average T=68 Days	<0.8	0.32	3.31	3.65	2.46	3.11	2.24	1.01	<0.2
Site M									
Average T=0 Days	<0.8	0.14	4.15	3.11	1.47	2.71	2.25	0.83	<0.2
Average T=68 Days	<0.8	0.29	5.12	3.69	1.28	3.69	1.30	0.50	<0.2
Site D									
Average T=0 Days	<0.8	<0.2	<0.3	<0.2	<0.4	<0.2	<0.2	<0.2	<0.2
Average T=68 Days	<0.8	<0.2	<0.3	<0.2	<0.4	<0.2	<0.2	<0.2	<0.2

Table A. 12 STS (Internal) and RTC (External) Quality Assurance Testing 23/12/2010 (all values as µg/L)

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
HAA 20 µg/L	20.6	20.6	19.4	18.9	22.5	12.8	9.86	12.6	12.9
HAA 20 µg/L	19.5	19.3	19.9	19.7	20	13	13.1	13	12.7
HAA 10 µg/L	10.7	11	10	10.4	9.84	9.16	9.35	8.85	8.71
HAA 5 µg/L	5.44	5.72	5.26	5.21	5.25	6.49	6.01	6.78	7.06
HAA 2 µg/L	2.56	2.15	1.97	2.27	2.53	2.6	2.72	3.36	3.31
HAA 1 µg/L	1.17	0.719	0.914	1.05	1.03	0.958	1.24	1.25	1.25
HAA 0.5 µg/L	0.0817	1.01	0.583	0.376	0.444	0.231	0.253	0.0469	0.256
HAA 0.2 µg/L	< 0	0.174	0.116	No Peak	No Peak	0.0858	< 0	< 0	< 0
HAA 0 µg/L	< 0	< 0	< 0	No Peak	No Peak	< 0	< 0	< 0	< 0
Bridgend Blank	< 0	< 0	0.635	0.194	0.574	< 0	No Peak	< 0	< 0
Bridgend AQC	< 0	8.58	7.49	0.015	0.188	7.46	No Peak	< 0	< 0
RTC	25.2	43.4*	19.8	16.4	72.9*	15.1*	< 0	< 0	< 0
RTC x 2	14.2	23	10.4	8.79	31.8*	10.9*	< 0	< 0	< 0
RTC x 3	5.61	8.95	4.19	3.63	11.1	6.8	< 0	< 0	< 0
Blank	< 0	< 0	0.00154	< 0	0.0185	< 0	< 0	< 0	< 0
Quality Control Blind Blank	< 0	< 0	0.64	0.19	0.57	< 0	No Peak	< 0	< 0
Quality Control Blind AQC	< 0	8.58	7.49	0.02	0.19	7.46	No Peak	< 0	< 0
Certified value	*NA*	*8.00*	*8.00*	*NA*	*NA*	*8.00*	*NA*	*NA*	*NA*
%Recovery	*NA*	*107%*	*94%*	*NA*	*NA*	*93%*	*NA*	*NA*	*NA*

Sample Name	MBAA	MCAA	DCAA	BCAA	DBAA	TCAA	BDCAA	CDBAA	TBAA
Pass/Fail	*NA*	Pass	Pass	*NA*	*NA*	Pass	*NA*	*NA*	*NA*
RTC Lot 016913	28.40	44.75	19.80	16.40	55.50	34.00	< 0	< 0	< 0
Certified value	*24.30*	*42.70*	*18.80*	*13.10*	*40.40*	*33.70*	*NA*	*NA*	*NA*
Acceptable Limits	*14.6 to 34.0*	*25.6 to 59.8*	*11.3 to 26.3*	*7.86 to 18.3*	*24.2 to 56.6*	*20.2 to 47.2*	*NA*	*NA*	*NA*
%Recovery	*117%*	*105%*	*105%*	*125%*	*137%*	*101%*	*NA*	*NA*	*NA*
Pass/Fail	Pass	Pass	Pass	Pass	Pass	Pass	*NA*	*NA*	*NA*

***** = Out of calibration range

NA= Not applicable, standard not in sample.